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MATHEMATICS

Some Remarks on the Marcinkiewicz-Orlicz Space

by
J. ALBRYCHT

Presented by S. MAZUR on October 25, 1955

Let M and N be a pair of functions complementary in the sense of Birnbaum-Orlicz ([1], p. 8, Def. 6). We shall denote by $\boldsymbol{M}$ the class of all real or complex-valued functions $y=y(t)$, $-\infty<t<+\infty$, measurable and integrable on every finite interval $(-T, +T)$ and such that

$$(1)\qquad \overline{\lim_{T\to\infty}}\frac{1}{2T}\int_{-T}^{T} M[|y(t)|]dt<\infty .$$

Writing N instead of M in (1), we obtain a complementary class which we indicate by $\overline{\boldsymbol{N}}$.

Classes $\overline{\boldsymbol{M}}$ and $\overline{\boldsymbol{N}}$ are convex sets but not in general linear sets; a necessary and sufficient condition for linearity of class $\overline{\boldsymbol{M}}(\overline{\boldsymbol{N}})$ is the fulfillment by the function $M(N)$ of the so-called Δ_2-condition (for definition of the latter, see [1], p. 36).

Now we denote by $\overline{\mathfrak{M}}$ the class of all real or complex-valued functions $x=x(t)$, $-\infty<t<+\infty$, measurable on every finite interval $(-T, +T)$ such that the product xy is integrable on every finite interval $(-T, +T)$ for every $y\in\overline{\boldsymbol{N}}$ and

$$\overline{\lim_{T\to\infty}}\frac{1}{2T}\left|\int_{-T}^{T} x(t)\,y(t)dt\right|<\infty .$$

It is evident that class $\overline{\mathfrak{M}}$ is linear.

In class $\overline{\mathfrak{M}}$ we define the pseudonorm $\|\ \|$ by formula

$$(2)\qquad \|x\|=\sup_{E}\left\{\overline{\lim_{T\to\infty}}\frac{1}{2T}\left|\int_{-T}^{T} x(t)y(t)dt\right|\right\},$$

where

$$E=\left\{y;\ y\in\overline{\boldsymbol{N}},\ \overline{\lim_{T\to\infty}}\frac{1}{2T}\int_{-T}^{T} N[|y(t)|]dt\leqslant 1\right\}.$$

We may put the sign of absolute value (module) in formula (2) under the integral. The pseudonorm thus obtained is equal to pseudonorm (2) but is sometimes more convenient in applications.

It is still possible to define, in class $\overline{\mathfrak{M}}$, a second pseudonorm $\| \|^*$; we define it by formula

$$\|x\|^* = \inf\left\{m;\ m > 0,\ \overline{\lim_{T\to\infty}} \frac{1}{2T}\int_{-T}^{T} M[|x(t)|/m]\,dt < 1\right\}^{*)}. \tag{3}$$

THEOREM 1. *If* $x \in \overline{\mathfrak{M}}$, *then* $\|x\|^* \leqslant \|x\| \leqslant 2\|x\|^*$.

THEOREM 2. *If* $x_n \in \overline{\mathfrak{M}} (n=1,2,\ldots)$ *and*

$$\lim_{n\to\infty} \|x_n\| = 0, \tag{*}$$

then

$$\lim_{n\to\infty}\left\{\overline{\lim_{T\to\infty}} \frac{1}{2T}\int_{-T}^{T} M[|x_n(t)|]\,dt\right\} = 0. \tag{**}$$

Under the additional assumption that function M fulfills the Δ_2-condition for $|u| \geqslant u_0 = 0$, (**) implies (*).

It is evident that $\overline{\mathbf{M}} \subset \overline{\mathfrak{M}}$; however, the reversed inclusion does not hold in general; nevertheless we can prove

THEOREM 3. *If* $x \in \overline{\mathfrak{M}}$, *then there exists a constant* $l > 0$ *such that* $lx \in \overline{\mathbf{M}}$, *and vice versa.*

THEOREM 4. *If the function* M *fulfills the* Δ_2*-condition, then* $\overline{\mathbf{M}} = \overline{\mathfrak{M}}$.

THEOREM 5. *A necessary and sufficient condition, for* $\overline{\mathfrak{M}}_2 \subset \overline{\mathfrak{M}}_1$, *is the existence of two constants* $k > 0$, $u_0 > 0$, *such that*

$$M_1(u) \leqslant M_2(ku) \quad \text{for} \quad |u| \geqslant u_0. \tag{4}$$

THEOREM 6. *If condition* (4) *is fulfilled, then*

$$\|x\|_1 \leqslant k\|x\|_2,$$

where $\| \|_1$ *and* $\| \|_2$ *respectively denote pseudonorms defined as in* (2) *in classes* $\overline{\mathfrak{M}}_1$ *and* $\overline{\mathfrak{M}}_2$.

Denoting by $\mathfrak{Q}$ a set of elements belonging to class $\overline{\mathfrak{M}}$, for which pseudonorm (2) is zero, we define a linear and normed *Marcinkiewicz-Orlicz space* as a quotient space

$$\overline{\mathfrak{M}}/\mathfrak{Q}.$$

*) The method of introducing the norms $\| \|$ and $\| \|^*$ is a generalisation of the method by which the norms are introduced in the so-called Orlicz space ([4], p. 210, [5], p. 302). Restricting our considerations to periodic functions of period p only, it can be proved that class $\overline{\mathfrak{M}}$ is identical with the so-called Orlicz space (for a periodic case).

THEOREM 7. *The Marcinkiewicz-Orlicz space is complete.*

THEOREM 8. *The Marcinkiewicz-Orlicz space is not separable.*

If the function M fulfills the Δ_2-condition, we can easily give the condition for compactness of a set of elements belonging to the Marcinkiewicz-Orlicz space; these conditions are similar to those given by Takahashi [2].

Putting $M(u)=|u|^p/p$, $N(v)=|v|^q/q$, $1/p+1/q=1$, we obtain an important example of the Marcinkiewicz-Orlicz space, first considered by Marcinkiewicz [3]. Theorem 7 is a generalisation of his well known result.

The Marcinkiewicz-Orlicz space finds applications in the theory of almost periodic functions in the generalised sense, the almost periodic functions of Besicovitch being a particular case of the latter.

Our next note will be devoted to this theory.

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MATHÉMATIQUE

Sur les coefficients tayloriens des fonctions univalentes

par
M. BIERNACKI

Présenté par K. KURATOWSKI le 29 Octobre 1955

Considérons la classe S des fonctions $f(z)=z+a_2z^2+\ldots+a_nz^n+\ldots$, holomorphes et univalentes dans le cercle $|z|<1$. G. M. Golousine a établi ([3], [4], [5] p. 207) l'inégalité

$$\big||a_{n+1}|-|a_n|\big|\leqslant Cn^{1/4}\log n \qquad (n=2,3,\ldots),$$

où C est une constante numérique, et il a ajouté que l'ordre de grandeur ainsi obtenu n'est certainement pas exact, bien que l'on ne réussisse pas à l'améliorer. Dans le cas particulier des fonctions $f(z)$ qui représentent le cercle $|z|<1$ sur un domaine étoilé par rapport à l'origine, Golousine a cependant établi l'inégalité $\big||a_{n+1}|-|a_n|\big|<C$, où C est une constante numérique [4]. Je me propose d'établir la proposition suivante:

THÉORÈME. *On a* $\big||a_{n+1}|-|a_n|\big|<C(\log n)^{3/2}$, $(n=2,3,\ldots)$, *où C est une constante numérique.*

Dans la démonstration je vais utiliser les résultats connus suivants:

I. Si $F(\zeta)=\zeta+b_0+b_1\zeta^{-1}+\ldots$ est holomorphe et univalente dans le domaine $|\zeta|>1$ et si $|\zeta_1|>1$, $|\zeta_2|>1$, on a (voir [3], [4] p. 9)

$$\left|\frac{F(\zeta_1)-F(\zeta_2)}{\zeta_1-\zeta_2}\right|\geqslant\sqrt{\left(1-\frac{1}{|\zeta_1|^2}\right)\left(1-\frac{1}{|\zeta_2|^2}\right)}. \tag{1}$$

II. Si $f(z)$ est holomorphe dans le cercle $|z|\leqslant r$, $n_r(\varrho,\varphi)$ est le nombre des racines de l'équation $f(z)=\varrho e^{i\varphi}$ qui sont contenues dans ce cercle et $M(r,\varphi)$ est le maximum de $|f(z)|$ lorsque $|z|=r$ et $\arg f(z)=\varphi$ on a pour $\lambda>0$ (voir [1], [2], [6]):

$$\frac{d}{dr}\int_0^{2\pi}|f(re^{i\theta})|^\lambda d\theta=\frac{\lambda^2}{r}\int_0^{2\pi}d\varphi\int_0^{M(r,\varphi)}n_r(\varrho,\varphi)\varrho^{\lambda-1}d\varrho. \tag{2}$$

III. Si $f(z)$ est une fonction de la classe S, on a pour $z=\varrho e^{i\theta}$ et $\varrho\leqslant r<1$:

$$(3) \qquad \int_0^r d\varrho \int_0^{2\pi} \left|\frac{zf'(z)}{f(z)}\right|^2 d\theta < A_1 \log\frac{1}{1-r},$$

$$(4) \qquad \int_0^{2\pi} \left|\frac{zf'(z)}{f(z)}\right|^2 d\theta < \frac{A_2}{1-r}\log\frac{1}{1-r},$$

où A_1 et A_2 (de même que dans la suite $A_3, A_4, \dots$) sont des constantes numériques [1].

IV. Si $f(z)$ est holomorphe dans le cercle $|z| \leqslant \varrho$, on a:

$$(5) \qquad \varrho\frac{d}{d\varrho}\int_0^{2\pi} |f|\, d\theta = \int_0^{\varrho} \left[u \int_0^{2\pi} \frac{|f'|^2}{|f|} d\theta\right] du \, (z = ue^{i\theta},\ 0 < u \leqslant \varrho)$$

(cas particulier de l'identité de Hardy-Stein, cf. p. ex. [7]).

$f(z)$ étant une fonction de la classe S, supposons qu'un nombre r, $0 < r < 1$, soit fixé et désignons par z_1 le point de la circonférence $|z| = (1+r)/2$, où $|f(z)|$ atteint son maximum. Considérons la fonction $\varphi(z) = (z - z_1) f(z)$. On a

$$\varphi(z) = c_1 z + \dots + c_n z^n + \dots, \quad \text{où} \quad c_n = a_{n-1} - z_1 a_n (n \geqslant 1).$$

Nous établirons le théorème en évaluant $|c_n|$ à l'aide d'une limite supérieure de l'intégrale

$$\int_0^{2\pi} |\varphi'(re^{i\theta})|\, d\theta.$$

En suivant l'idée de Golousine appliquons l'inégalité (1) à la fonction $1/f(1/\zeta)$ et aux points $\zeta_1 = 1/z_1$ et $\zeta_2 = 1/z$, où z est un point quelconque du cercle $|z| \leqslant r$. On obtient ainsi les inégalités

$$\left|\frac{z_1 - z}{zz_1}\right| \sqrt{(1-|z_1|^2)(1-|z|^2)} \leqslant \left|\frac{1}{f(z_1)} - \frac{1}{f(z)}\right| \leqslant \frac{2}{|f(z)|},$$

d'où, en posant $|z| = \varrho \leqslant r$:

$$(6) \qquad |\varphi(z)| \leqslant 2\sqrt{2}(1-\varrho)^{-1/2}(1-r)^{-1/2}.$$

On a d'autre part

$$\frac{z\varphi'(z)}{\varphi(z)} = \frac{zf'(z)}{f(z)} + \frac{z}{z - z_1}$$

et des considérations élémentaires montrent que l'on a dans le cercle $|z| \leqslant r$ et si $|z_1| \geqslant 1/2$:

$$\int_0^r d\varrho \int_0^{2\pi} \left|\frac{z}{z - z_1}\right|^2 d\theta < A_3 \log\frac{1}{1-r};$$

donc, en tenant compte de (3) et de l'inégalité $(a+b)^2 \leqslant 2(a^2+b^2)$, on a

$$\int_0^r d\varrho \int_0^{2\pi} \left|\frac{z\varphi'}{\varphi}\right|^2 d\theta < A_4 \log\frac{1}{1-r}. \tag{7}$$

Or, en vertu des théorèmes classiques, $|z\varphi'^2| : |\varphi|$ est borné par un nombre qui ne dépend ni de z_1, ni du choix d'une fonction $f(z)$ particulière dans un cercle $|z| \leqslant \varrho_0$, où ϱ_0 est une constante numérique arbitraire $(0 < \varrho_0 < 1/2)$ pourvu que $|z_1| \geqslant 1/2$. Il résulte donc de (5), (6) et (7) que l'on a pour $\varrho_0 < \varrho \leqslant r$ $(z = ue^{i\theta})$:

$$\begin{aligned}\frac{d}{d\varrho}\int_0^{2\pi}|\varphi|\, d\theta &< \frac{1}{\varrho_0}\int_0^{\varrho_0} u\left[\int_0^{2\pi}\frac{|\varphi'|^2}{|\varphi|}\, d\theta\right] du + \\ &+ \frac{1}{\varrho_0^2}\int_{\varrho_0}^{\varrho}\left[\int_0^{2\pi}\left|\frac{z\varphi'}{\varphi}\right|^2 |\varphi|\, d\theta\right] du < A_5 (1-\varrho)^{-1/2}(1-r)^{-1/2}\log\frac{1}{1-r}.\end{aligned} \tag{8}$$

Considérons maintenant l'égalité (2) et l'égalité obtenue en y remplaçant λ par μ $(\lambda > \mu > 0)$. En divisant ces égalités membre à membre on obtient, en remplaçant r par ϱ et en posant $M(\varrho) = \underset{|z| \leqslant \varrho}{\operatorname{Max}} |f(z)|$:

$$\frac{d}{d\varrho}\int_0^{2\pi}|f|^\lambda d\theta : \frac{d}{d\varrho}\int_0^{2\pi}|f|^\mu d\theta \leqslant \frac{\lambda^2}{\mu^2}[M(\varrho)]^{\lambda-\mu},$$

d'où, en intégrant entre les limites 0 et r,

$$\int_0^{2\pi} |f(re^{i\theta})|^\lambda d\theta \leqslant 2\pi |f(0)|^\lambda + \frac{\lambda^2}{\mu^2}\int_0^r \left\{[M(\varrho)]^{\lambda-\mu}\frac{d}{d\varrho}\int_0^{2\pi}|f(\varrho e^{i\theta})|^\mu d\theta\right\} d\varrho \tag{A}$$

$$(\lambda > \mu > 0).$$

Cette inégalité, *valable pour toute fonction holomorphe dans le cercle* $|z| \leqslant r$, présente peut-être de l'intérêt en elle-même. En posant dans (A) $\lambda = 2$, $\mu = 1$, en y remplaçant $f(z)$ par $\varphi(z)$, et en remarquant que pour $\varrho \leqslant \varrho_0$ l'expression sous le signe de l'intégrale dans (A) est plus petite qu'une constante numérique, enfin en tenant compte de (6) et (8), on obtient l'inégalité:

$$\int_0^{2\pi} |\varphi(re^{i\theta})|^2 d\theta \leqslant A_6 + \frac{4\sqrt{2}A_5}{1-r}\log\left(\frac{1}{1-r}\right)\cdot\int_{\varrho_0}^r \frac{d\varrho}{1-\varrho} < \frac{A_7}{1-r}\left(\log\frac{1}{1-r}\right)^2. \tag{9}$$

Or, en utilisant l'inégalité de Bouniakowski-Schwarz on a

$$\int_0^{2\pi}|\varphi'(re^{i\theta})|\, d\theta = \int_0^{2\pi}\left|\frac{\varphi'}{\varphi}\right|\cdot|\varphi|\, d\theta \leqslant \frac{1}{\varrho_0}\sqrt{\int_0^{2\pi}\left|\frac{z\varphi'}{\varphi}\right|^2 d\theta \cdot \int_0^{2\pi}|\varphi|^2 d\theta}.$$

Donc, en tenant compte de (4) et de (9),

$$\int_0^{2\pi} |\varphi'(re^{i\theta})|\, d\theta < \frac{A_8}{1-r}\left(\log\frac{1}{1-r}\right)^{3/2}.$$

Cependant $\varphi(z) = \sum_{n=1}^{\infty} c_n z^n$; donc, en posant $r = 1 - \dfrac{1}{n}$ $(n \geqslant 2)$, on a $n|c_n| \leqslant A_9 n (\log n)^{3/2}$, c'est-à-dire que si $f(z) = z + \ldots + a_n z^n + \ldots$, on a $|a_{n-1} - z_1 a_n| < A_9 (\log n)^{3/2}$.

Or $|z_1| = (1+r)/2 = 1 - 1/2n$; donc a fortiori

$$\left| |a_{n-1}| - \left(1 - \frac{1}{2n}\right)|a_n| \right| < A_9 (\log n)^{3/2} \quad \text{et} \quad \big| |a_{n-1}| - |a_n| \big| < A_9 (\log n)^{3/2} + |a_n|/2n.$$

Comme $|a_n|/n < e$, le théorème énoncé est établi.

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MATHÉMATIQUE

Étude de la solution fondamentale de l'équation parabolique

par
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Présenté par K. KURATOWSKI le 14 Novembre 1955

Considérons l'équation aux dérivées partielles du type parabolique de la forme

$$(1)\qquad \Psi[u]=\sum_{\alpha,\beta=1}^{n} a_{\alpha\beta}(x_1,\dots,x_n;t)\frac{\partial^2 u}{\partial x_\alpha \partial x_\beta}+\sum_{\alpha=1}^{n} b_\alpha(x_1,\dots,x_n;t)\frac{\partial u}{\partial x_\alpha}+ c(x_1,\dots,x_n;t)\,u-\frac{\partial u}{\partial t}=0,$$

où les coefficients $a_{\alpha\beta}$, b_α et c sont des fonctions de $n+1$ variables $(x_1,\dots,x_n;t)$ déterminées dans un domaine borné et mesurable Ω dans l'espace euclidien à n dimensions et dans l'intervalle $0\leqslant t\leqslant T$. Admettons que la forme quadratique

$$(2)\qquad \sum_{\alpha,\beta=1}^{n} a_{\alpha\beta}\, x_\alpha x_\beta$$

est définie positive dans le domaine $[\Omega,(0,T)]$.

La première idée concernant la recherche de la solution fondamentale de l'équation (1) est due à Giraud [1]. Plus tard, Dressel [2] a étudié la solution fondamentale de l'équation (1), mais sous l'hypothèse très restrictive, à savoir que les coefficients $a_{\alpha\beta}$ sont des fonctions admettant les dérivées secondes. Dans cette communication nous présenterons les résultats de nos recherches concernant la solution fondamentale de l'équation (1) sous l'hypothèse plus générale suivante: les coefficients $a_{\alpha\beta}(A,t)$, $b_\alpha(A,t)$ et $c(A,t)$ sont des fonctions continues de l'ensemble des variables dans la région fermée $[\Omega,(0,T)]$ et ils satisfont par rapport aux variables spatiales $A(x_1,\dots,x_n)$ à la condition d'Hölder de la forme

$$(3)\qquad |a_{\alpha\beta}(A,t)-a_{\alpha\beta}(A_1,t)|<\text{const}\colon r_{AA_1}^{h}\qquad \text{pour}\qquad 0<h\leqslant 1$$

(les inégalités admises pour b_α et c étant analogues), où r_{AA_1} est la distance pythagoréenne entre les points A et A_1. Dans le théorème 5, la

condition d'Hölder est supposée aussi par rapport à la variable t, mais pour les coefficients $a_{\alpha\beta}(A,t)$ seulement.

THÉORÈME 1. *Si les coefficients* $a_{\alpha\beta}(A,t)$ *et la densité* $\varrho(A,t)$ *sont des fonctions continues par rapport à l'ensemble de variables* $(x_1,\dots,x_n;\,t)$ *dans la région fermée* $[A \in \Omega;\ 0 \leqslant t \leqslant T]$, *l'intégrale de Weierstrass généralisée* *)

$$J(A,t,\tau) = \iiint\limits_{\Omega} w^{B,\tau}(A,t;\,B,\tau)\,\varrho(B,\tau)\,dv_B \tag{4}$$

est régulière, continue pour $0 \leqslant \tau < t \leqslant T$ *et tend uniformément à la limite*

$$\lim_{\tau\to t} J(A,t,\tau) = \frac{(2\sqrt{\pi})^n}{\sqrt{\det|a^{\alpha\beta}(A,t)|}}\,\varrho(A,t) \tag{5}$$

en tout point intérieur A *du domaine* Ω *et pour* $0 < t \leqslant T$.

La fonction w dans (4) est définie par les formules

$$w^{M,\tau}(A,t;\,B,\tau) = (t-\tau)^{-\frac{n}{2}} \exp\left[-\frac{\vartheta^{M,\tau}(A,B)}{4(t-\tau)}\right], \tag{6}$$

$$\vartheta^{M,\tau}(A,B) = \sum_{\alpha,\beta=1}^{n} a^{\alpha\beta}(M,\tau)(x_\alpha - \xi_\alpha)(x_\beta - \xi_\beta),$$

où $a^{\alpha\beta}(M,\tau)$ désignent les éléments de la matrice *inverse* de $\|a_{\alpha\beta}(M,\tau)\|$ et M est un point arbitrairement fixé dans le domaine Ω. La fonction (6) est déterminée pour tout couple de points $A(x_1,\dots,x_n)$, $B(\xi_1,\dots,\xi_n)$ du domaine fermé Ω et pour tout couple τ, t où $\tau < t$ dans l'intervalle $[0,T]$.

THÉORÈME 2. *Si les coefficients* $a_{\alpha\beta}(A,t)$ *et la densité* $\varrho(A,t)$ *sont des fonctions continues dans la région fermée* $[\Omega;\,(0,T)]$ *et satisfont à la condition d'Hölder* (3) *par rapport aux variables spatiales, le quasi-potentiel*

$$V(A,t) = \int_0^t \iiint\limits_{\Omega} w^{B,\tau}(A,t;\,B,\tau)\,\varrho(B,\tau)\,dv_B\,d\tau \tag{7}$$

admet les secondes dérivées spatiales continues, données par la formule

$$V_{x_\alpha x_\beta}(A,t) = \int_0^t \iiint\limits_{\Omega} w^{B,\tau}_{x_\alpha x_\beta}(A,t;\,B,\tau)\,\varrho(B,\tau)\,dv_\beta\,d\tau, \tag{8}$$

et la dérivée par rapport à t, *donnée par la formule*

$$V_t(A,t) = \int_0^t \iiint\limits_{\Omega} w^{B,\tau}_t(A,t;\,B,\tau)\,\varrho(B,\tau)\,dv_B\,d\tau + \frac{(2\sqrt{\pi})^n}{\sqrt{\det|a^{\alpha\beta}(A,t)|}}\,\varrho(A,t). \tag{9}$$

*) L'intégrale triple désignant ici celle de volume même dans l'espace à $n > 3$ dimensions.

Les intégrales spatiales dans les formules (8), (9) sont régulières et admettent une limitation à singularité faible

$$(10)\qquad |J_{x_\alpha x_\beta}(A,t,\tau)| < \frac{c_A}{(t-\tau)^\mu},$$

μ étant choisi dans l'intervalle ouvert $\left(1-\frac{h}{2},1\right)$.

THÉORÈME 3. *Si les coefficients $a_{\alpha\beta}(A,t)$ et la densité $\varrho(A,t)$ satisfont aux hypothèses du théorème 2, les dérivées du quasi-potentiel* (7) *satisfont à l'équation*

$$(11)\qquad \sum_{\alpha,\beta=1}^{n} a_{\alpha\beta}(A,t)V_{x_\alpha x_\beta}(A,t)-V_t(A,t)= -\frac{(2\sqrt{\pi})^n}{\sqrt{\det|a^{\alpha\beta}(A,t)|}}\varrho(A,t)+$$
$$+\int_0^t\iiint_\Omega \sum_{\alpha,\beta=1}^{n}[a_{\alpha\beta}(A,t)-a_{\alpha\beta}(B,\tau)]w^{B,\tau}_{x_\alpha x_\beta}(A,t;\, B,\tau)\,\varrho(B,\tau)\,dv_B d\tau$$

en tout point intérieur A du domaine Ω pour $0<t<T$. L'intégrale spatiale est régulière pour $\tau<t$ et celle par rapport à la variable t est impropre, mais admet une singularité faible limitée par (10).

La solution fondamentale de l'équation (1) est déterminée par la formule

$$(12)\qquad \Gamma(A,t;\,B,\tau)= w^{B,\tau}(A,t;\,B,\tau)+\int_\tau^t\iiint_{\Omega'} w^{M,\theta}(A,t;\,M,\theta)\Phi(M,\theta;\,B,\tau)\,dv_B d\theta,$$

où la fonction Φ est une solution de l'équation intégrale

$$(13)\qquad \Phi(A,t;\,B,\tau)= f(A,t;\,B,\tau)+\lambda\int_\tau^t\iiint_{\Omega'} N(A,t;\,M,\theta)\Phi(M,\theta;\,B,\tau)\,dv_M d\theta,$$

dans laquelle on a posé

$$(14)\qquad \begin{aligned} N(A,t;\,M,\theta)&=\sqrt{\det|a^{\alpha\beta}(A,t)|}\,\hat{\Psi}_{A,t}[w^{M,\theta}(A,t;\,M,\theta)],\quad \lambda=(2\sqrt{\pi})^{-n}\\ f(A,t;\,B,\tau)&=\lambda\sqrt{\det|a^{\alpha\beta}(A,t)|}\,\hat{\Psi}_{A,t}[w^{B,\tau}(A,t;\,B,\tau)].\end{aligned}$$

B et τ jouent ici le rôle de paramètres ($B\neq A$; $\tau<t$), Ω' est un domaine arbitraire borné et mesurable contenant Ω et les coefficients $a_{\alpha\beta}(A,t)$ sont supposés prolongés dans le domaine Ω' de façon qu'ils satisfassent aux hypothèses du théorème 2. Le noyau de l'équation (13) n'est pas borné, mais en admettant la condition d'Hölder pour les fonctions $a_{\alpha\beta}$ relativement aussi à la variable t, on obtient une limitation aux singu-

larités faibles:

$$(15) \qquad |N(A,t;\,M,\theta)| < \frac{\text{const}}{(t-\theta)^{\mu}} \cdot \frac{1}{r_{AM}^{n+2-2\mu-h_1}},$$

μ étant choisi dans l'intervalle ouvert $\left(1-\frac{h_1}{2},1\right)$ et h_1 étant le plus petit des deux nombres h et $2h'$ dont h' est l'exposant d'Hölder pour les coefficients $a_{\alpha\beta}(A,t)$ correspondant à la variable t.

La limitation de la forme (15) concerne aussi la fonction $f(A,t;\,B,\tau)$. Vu la limitation (15), on obtient la solution de l'équation (13) dans la forme

$$(16) \qquad \Phi(A,t;\,B,\tau) = f(A,t;\,B,\tau) + \lambda \int_{\tau}^{t} \int\int_{\Omega'}\int \mathfrak{N}(A,t;M,\theta)\, f(M,\theta;\,B,\tau)\, dv_M d\theta,$$

où le noyau résolvant $\mathfrak{N}$ est la somme de la série

$$(17) \qquad \mathfrak{N}(A,t;\,M,\theta) = N(A,t;\,M,\theta) + \sum_{\nu=1}^{\infty} \lambda^{\nu} N_{\nu}(A,t;\,M,\theta);$$

les noyaux itérés satisfont à l'inégalité

$$(18) \qquad |N_{\nu_0+m}(A,t;\,M,\theta)| < \frac{2g_1}{mh_1}\, \frac{[g_2\Gamma(1-\mu)(t-\theta)^{1-\mu}]^m}{\Gamma[m(1-\mu)]}$$

assurant la convergence absolue et uniforme de la série (17); ν_0 est l'indice du premier noyau borné, enfin g_1 et g_2 sont des constantes. La solution (16) a la propriété importante qui suit.

THÉORÈME 4. *La solution* (16) *de l'équation* (13) *satisfait à la condition d'Hölder de la forme*

$$(19) \qquad |\Phi(A,t;\,B,\tau) - \Phi(A_1,t;\,B,\tau)| < \frac{\text{const}}{\inf r_{AB}^{n+3}}\, r_{AA_1}^{h^*}$$

dans tout domaine fermé Ω^* situé à l'intérieur du domaine Ω' et n'en contenant pas de point B. La constante dans l'inégalité (19) *ne dépend pas des variables τ et t. Le symbole* $\inf r_{AB}$ *désigne la borne inférieure positive de la distance entre le point fixé B et le point variable A du domaine Ω^*. Enfin, h^* est un nombre positif arbitraire, inférieur au nombre h_1.*

Le théorème 4 permet de conclure que la fonction représentée par la formule (12) satisfait à l'équation donnée (1) et tout point intérieur A de Ω', différent du point B et pour $0<\tau<t\leqslant T$.

On a le théorème suivant sur le potentiel de la charge spatiale:

THÉORÈME 5. *Admettons que les coefficients $a_{\alpha\beta}$ satisfont à la condition d'Hölder par rapport aux variables $(x_1,\dots,x_n;\,t)$, que les fonctions continues b_α et c lui satisfont par rapport aux variables spatiales dans le domaine Ω et qu'en outre la fonction $\varrho(A,t)$, continue dans le domaine fermé Ω,*

satisfait à cette condition par rapport aux variables spatiales dans un domaine $\Omega^* \subset \Omega$. Alors le potentiel de la charge spatiale

$$U(A,t) = \int_0^t \iiint_\Omega \Gamma(A,t;\, B,\tau)\, \varrho(B,\tau)\, dv_B\, d\tau \tag{20}$$

satisfait à l'équation généralisée de Poisson

$$\hat{\Psi}[U(A,t)] = -\frac{(2\sqrt{\pi})^n}{\sqrt{\det|a^{\alpha\beta}(A,t)|}}\, \varrho(A,t) \tag{21}$$

en tout point intérieur A du domaine Ω^* pour $0 < t \leqslant T$.

Pour les autres détails et démonstrations, voir sous le même titre: Ricerche di Matematica, Napoli, 5 (1956).

INSTITUT MATHÉMATIQUE DE L'ACADÉMIE POLONAISE DES SCIENCES

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MATHEMATICS

The Strong Law of Large Numbers for Generalized Random Variables

by

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Presented by H. STEINHAUS on November 19, 1955

Let B be a Banach space with a base, and $\mathfrak{B}$ the σ-algebra of Borel subsets of B. Let $\Omega \neq \theta$ be an abstract space and

(1) $$S_1(\omega),\ S_2(\omega), \ldots$$

a sequence of transforms on Ω into B. Let $\mathcal{S}$ be the smallest σ-algebra of subsets of Ω, generated by the class

$$\left\{\{\omega : S_n(\omega) \in G\} : G \in \mathfrak{B},\ n = 1, 2, \ldots\right\}.$$

We shall further suppose that Ω is sufficiently large, i. e., if ω ranges over Ω and f ranges over the space of all bounded linear functionals on B, then

(2) $$fS_1(\omega), fS_2(\omega), \ldots$$

ranges over all sequences of real numbers.

A transform $S(\omega)$ is said to be a generalized random variable, if $S(\omega)$ is a measurable transform on $(\Omega, \mathcal{S})$ into $(B, \mathfrak{B})$. By an expectation of a generalized random variable we always understand its Pettis integral with respect to a probability measure μ defined on $\mathcal{S}$, and almost sure property always means that the set defined by this property has outer measure one.

A useful tool for proving various "almost sure convergence" theorems is the following

Almost sure weak convergence Theorem. *Let* (1) *be a sequence of generalized random variables. Then* (1) *converges weakly to* $\Theta \in B$ *almost surely if, and only if, for every bounded linear functional* f *the sequence* (2) *of usual random variables converges to* 0 *almost surely. In other words,*

(3) $$\mu\{\omega : fS_n(\omega) \to 0\} = 1 \quad \textit{for every} \quad f \in B^*$$

is equivalent to

$$\bar{\mu}\{\omega: S_n(\omega) \xrightarrow{\text{weakly}} \Theta\} = \bar{\mu}(\bigcap_{f \in B^*} \{\omega: fS_n(\omega) \to 0\}) = 1,$$

where B^* denotes the first adjoint space of the space B.

The essential facts, the proof is based on, are the structure of the σ-algebra $\mathcal{S}$ and the Špaček regularity theorem [1].

In a similar way can be proved the

Almost sure strong convergence Theorem. *Let* (1) *be a sequence of generalized random variables.*

Then (1) *converges strongly to $\Theta \in B$ almost surely if, and only if, for every bounded linear functional f the sequence* (2) *converges to* 0 *almost surely, and the set*

$$K(\omega) = \bigcup_{n=1}^{\infty} \{S_n(\omega)\} \tag{4}$$

is almost surely compact.

In other words, (3) *together with*

$$\bar{\mu}\{\omega: K(\omega) \text{ is compact }\} = 1,$$

is equivalent to

$$\bar{\mu}\{\omega: S_n(\omega) \xrightarrow{\text{strongly}} \Theta\} = 1.$$

A number of useful theorems follow from our two basic theorems; here we state only some of them.

The following theorem is sometimes called the strong law of large numbers for equal distributed random variables.

Theorem 1. *Let* (1) *be a sequence of mutually independent generalized random variables with the same distribution.*

Then a necessary and sufficient condition for the validity of the strong law of large numbers for strong convergence is the existence of expectation and the compactness of the set $S_1(\Omega)$.

Another consequence of the almost sure strong convergence theorem is

Theorem 2. *If* (1) *is a sequence of mutually independent generalized random variables such that*

$$\begin{gathered} \int_{\Omega} S_n(\omega) d\mu = 0 \quad \textit{for every} \quad n, \\ \sum_{n=1}^{\infty} \int_{\Omega} \|S_n(\omega)\|^2 d\mu < \infty, \end{gathered} \tag{5}$$

and the set (4) *is almost surely compact, then the series*

$$\sum_{n=1}^{\infty} S_n(\omega) \tag{6}$$

converges strongly almost surely.

Conditions for almost sure convergence of sums of independent random variables are obtained by means of centerings at expectations. In the case of dependent generalized random variables, as well as in the theory of usual random variables, the centerings at conditional expectations given the predecessors are used, and the orthogonality property remains valid. Thus

THEOREM 3. *Let* (1) *be a sequence of generalized random variables such that the conditional expectations* $T_n(\omega)$ *of* $S_n(\omega)$, *given* $S_1(\omega), S_2(\omega), \ldots, S_{n-1}(\omega)$, *exist.*

If (5) *holds and the series* $\sum_{n=1}^{\infty} T_n(\omega)$ *converges weakly almost surely, then the series* (6) *converges weakly almost surely.*

The complete proofs of the above theorems, as well as other similar results will appear in a paper in the Czechoslovak Mathematical Journal. The relation between our results and that of Fortet and Mourier will be stated in this forthcoming paper too.

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THEORETICAL PHYSICS

On the Equation for a Distinguished Component of the State Vector

by

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Presented by W. RUBINOWICZ on November 12, 1955

In the first part of this paper we discuss the problem of deriving an equation for a distinguished component of the state vector from the state equation of an arbitrary quantized system. A non-homogeneous equation, integro-differential with respect to time, is obtained, in which the non-homogeneity is determined by the initial values of all components of the state vector other than the distinguished one. In the case of these components vanishing at a particular time the integro-differential equation becomes homogeneous and, when the initial time is removed into $-\infty$, may be replaced by a stationary equation independent of time and containing an interaction operator which is a function of the energy eigenvalue (non-linear energy eigenvalue problem). Close expressions are obtained for the kernels of integro-differential and stationary equations, valid for arbitrary values of the interaction constant.

In the second part the integro-differential equation is replaced by an equivalent equation purely differential with respect to time. In the homogeneous case this equation has the form of a Schrödinger equation (in the time-independent case — of a linear energy eigenvalue problem) with a complex "potential". The imaginary part of this "potential" is due to the instability of the distinguished state of the system and determines the life-time of this state.

The theory presented in this paper comprises in particular the following cases: the theory of bound states of particles and the theory of scattering, if we are interested (as in the Feshbach-Porter-Weisskopf theory) in the capture of incoming particles from an initial state.

Introduction

Consider an arbitrary quantized system consisting of some parts interacting with each other and possibly with an external system, which

has to be fixed in time. Assume the total energy of the system to have the form $\overset{0}{H}+\overset{1}{H}$, where $\overset{0}{H}$ denotes the energy of the free parts and, possibly, the interaction with the external system, and $\overset{1}{H}$ denotes the energy of mutual interaction of the parts. Thus, the equation for the state vector of the system in the Schrödinger picture has the form:

$$\left(i\hbar\frac{\partial}{\partial t}-\overset{0}{H}\right)\Psi=\overset{1}{H}\Psi. \tag{1}$$

There are several important problems in the quantum theory, which may be described by means of a distinguished component of the state vector Ψ. E. g.:

1. Problems concerning N_0 particles of two interacting fields can be described by the component of the state vector Ψ corresponding to N_0 particles.

2. The problem of the scattering of a particle on a scatterer which is in state $|a_0>$ may be described by the component of the state vector Ψ corresponding to the scatterer in state $|a_0>$ and also to the particle.

The aim of the present paper is to derive from the state equation (1) an equation for a distinguished component of the state vector Ψ. First, we must obtain an equation for this component integro-differential with respect to time. Next, we must transform it into an equivalent equation, purely differential with respect to time.

In some cases this will have the form of a Schrödinger equation with a complex "potential". Both the above equations expressed in terms of representatives become integral equations with respect to new variables. We shall obtain closed expressions for the kernels of these equations which will be valid for arbitrary values of the interactions constant.

The integro-differential equation

Let us denote by $P_{||}$ the projection operator, which, acting on the state vector Ψ, chooses its distinguished component $\Psi_{||}$. The projection operator $P_{\perp}=1-P_{||}$, acting on the state vector, produces the component $\Psi_{\perp}=\Psi-\Psi_{||}$.

Thus, we have $\Psi=\Psi_{||}+\Psi_{\perp}$, where $\Psi_{||}=P_{||}\Psi$ and $\Psi_{\perp}=P_{\perp}\Psi$. We note the relations

$$P_{||}+P_{\perp}=1, \quad P_{||}^2=P_{||}, \quad P_{\perp}^2=P_{\perp}, \quad P_{||}P_{\perp}=P_{\perp}P_{||}=0. \tag{2}$$

Assume the operators $P_{||}$ and $P_{\perp}$ to commute with $\overset{0}{H}$.

In the first example, given in the Introduction, the projection operators have the form:

$$P_{||}=\sum_{\lambda(N_0)}|\lambda(N_0)\rangle\langle\lambda(N_0)|, \qquad P_{\perp}=\sum_{N\neq N_0}\sum_{\lambda(N)}|\lambda(N)\rangle\langle\lambda(N)|.$$

where $\lambda(N)$ denotes a set of eigenvalues of a complete system of commuting observables determining the states of $N=(f,a,b)$, particles, where f, a, and b are the numbers of fermions, antifermions and bosons respectively. In particular, $\lambda(N)$ may be a set of eigenvalues of the position or momentum operators of the N particles. In the second example we have:

$$P_{\parallel}=\sum_{\lambda(1)}|\lambda(1)\,a_0\rangle\langle\lambda(1)\,a_0|, \qquad P_{\perp}=\sum_{\lambda(1)}\sum_{a\neq a_0}|\lambda(1)\,a\rangle\langle\lambda(1)\,a|,$$

where $\lambda(1)$ denotes a set of eigenvalues for a complete system of commuting observables determining the state of a particle, and a denotes a set of eigenvalues for a complete system determining the energy eigenstates of the scatterer. In particular, $\lambda(1)$ may be an eigenvalue of the position or momentum operator of the particle. In both the above examples $P_{\parallel}$ and $P_{\perp}$ commute with $\overset{0}{H}$.

In the second instance we are interested in the transition of an incoming particle from an initial state to all other states, due to inelastic scattering and to the forming of compound states. When describing the influence of the forming of compound states on elastic and inelastic scattering, we consider projection operators with the form:

$$P_{\parallel}=\sum_{s}|s\rangle\langle s|, \qquad P_{\perp}=\sum_{c}|c\rangle\langle c|,$$

where the labels s and c correspond, respectively, to the scattering and to the compound eigenstates of the Hamiltonian $\overset{0}{H}$ in which the interaction forming compound states is included, whereas $\overset{1}{H}$ denotes the scattering interaction.

Let us transform equation (1) for the state vector in the Schrödinger picture into a new picture by means of the following unitary transformation

$$\Psi_F(t)=e^{\frac{i}{\hbar}(\overset{0}{H}+P_{\parallel}\overset{1}{H}P_{\parallel}+P_{\perp}\overset{1}{H}P_{\perp})(t-t_0)}\,\Psi(t); \tag{3}$$

$$O_F(t)=e^{\frac{i}{\hbar}(\overset{0}{H}+P_{\parallel}\overset{1}{H}P_{\parallel}+P_{\perp}\overset{1}{H}P_{\perp})(t-t_0)}\,O\,e^{-\frac{i}{\hbar}(\overset{0}{H}+P_{\parallel}\overset{1}{H}P_{\parallel}+P_{\perp}\overset{1}{H}P_{\perp})(t-t_0)}.$$

We note that the operators $P_{\parallel}$ and $P_{\perp}$ commute with $\overset{0}{H}+P_{\parallel}\overset{1}{H}P_{\parallel}+P_{\perp}\overset{1}{H}P_{\perp}$.

From this fact and the relation

$$\overset{1}{H}=P_{\parallel}\overset{1}{H}P_{\parallel}+P_{\perp}\overset{1}{H}P_{\perp}+P_{\parallel}\overset{1}{H}P_{\perp}+P_{\perp}\overset{1}{H}P_{\parallel},$$

it follows that the equation for the state vector in the new picture takes the form

$$i\hbar\frac{\partial\Psi_F}{\partial t}=(P_{\parallel}\overset{1}{H}_F(t)P_{\perp}+P_{\perp}\overset{1}{H}_F(t)P_{\parallel})\Psi_F. \tag{4}$$

Multiplying this equation by $P_{\parallel}$ and $P_{\perp}$ respectively, we get an equivalent system of two equations

$$
(5)\qquad
\begin{aligned}
i\hbar\frac{\partial\Psi_{F\parallel}}{\partial t}&=P_{\parallel}\overset{1}{H}_F\Psi_{F\perp},\\
i\hbar\frac{\partial\Psi_{F\perp}}{\partial t}&=P_{\perp}\overset{1}{H}_F\Psi_{F\parallel},
\end{aligned}
$$

where $\Psi_{F\parallel}=P_{\parallel}\Psi_F=\Psi_{\parallel F}$, $\Psi_{F\perp}=P_{\perp}\Psi_F=\Psi_{\perp F}$. Eliminating now from the first equation (5) the component $\Psi_{F\perp}$ by means of the second equation, we get

$$
(6)\qquad i\hbar\frac{\partial\Psi_{F\parallel}(t)}{\partial t}=P_{\parallel}\overset{1}{H}_F(t)P_{\perp}\Psi_{\perp}(t_0)-\frac{i}{\hbar}\int_{t_0}^{\infty}dt'K_F(t,t')\Psi_{F\parallel}(t'),
$$

where

$$
(7)\qquad K_F(t,t')=P_{\parallel}\overset{1}{H}_F(t)P_{\perp}\theta^{+}(t-t')P_{\perp}H_F(t')P_{\parallel}.
$$

Going back to the Schrödinger picture and making use of the equalities $P_{\perp}\overset{1}{H}P_{\perp}\Psi_{\parallel}=0$ and $P_{\parallel}\overset{1}{H}P_{\parallel}\Psi_{\perp}=0$, we get for the component $\Psi_{\parallel}(t)$ of the state vector $\Psi(t)$ in the Schrödinger picture the following equation

$$
(8)\qquad \left(i\hbar\frac{\partial}{\partial t}-\overset{0}{H}-P_{\parallel}\overset{1}{H}P_{\parallel}\right)\Psi_{\parallel}(t)=P_{\parallel}\overset{1}{H}P_{\perp}e^{-\frac{i}{\hbar}(\overset{0}{H}+P_{\perp}\overset{1}{H}P_{\perp})(t-t_0)}\Psi_{\perp}(t_0)-
$$
$$
-\frac{i}{\hbar}\int_{t_0}^{\infty}dt'K(t-t')\Psi(t'),
$$

where

$$
(9)\qquad K(t-t')=P_{\parallel}\overset{1}{H}P_{\perp}\theta^{+}(t-t')e^{-\frac{i}{\hbar}(\overset{0}{H}+P_{\perp}\overset{1}{H}P)(t-t_0)}P_{\perp}\overset{1}{H}P_{\parallel}.
$$

In the case when $\Psi_{\perp}(t_0)=0$ and $t_0\to-\infty$ we may go over from (8) to the time-independent equation by means of the substitution

$$
\Psi_{\parallel E}(t)=\Phi_{\parallel E}\,e^{-\frac{i}{\hbar}Et},\qquad\text{thus}\qquad \Psi_{\parallel}(t)=\sum_E\Phi_{\parallel E}\,e^{-\frac{i}{\hbar}Et}c_E.
$$

In this way we get the equation

$$
(10)\qquad (E-\overset{0}{H}-P_{\parallel}\overset{1}{H}P_{\parallel})\Phi_{\parallel E}=U(E)\Phi_{\parallel E},
$$

where

$$
(11)\qquad U(E)=-\frac{i}{\hbar}\int_{-\infty}^{\infty}dt\,K(t)e^{\frac{i}{\hbar}Et}=
$$
$$
=P_{\parallel}\overset{1}{H}P_{\perp}\left[P\frac{1}{E-\overset{0}{H}-P_{\perp}\overset{1}{H}P}-i\pi\delta(E-\overset{0}{H}-P_{\perp}\overset{1}{H}P_{\perp})\right].
$$

Here the symbol P denotes that, upon integration, one has to take Cauchy's principal value of the integral. It is possible to show that equa-

tion (10) is identical with the equation for the component $\Phi_{\parallel E}=P_{\parallel}\Phi_E$, obtained from the eigenvalue problem for the total energy

$$(E-\overset{0}{H})\Phi_E=\overset{1}{H}\Phi_E \tag{12}$$

(where $\Phi_E=|E\rangle$) by elimination of the component $\Phi_{\perp E}=P_{\perp}\Phi_E$. It follows that the parameter E in equation (10) represents an eigenvalue of the total energy of the system. However, owing to the dependence of $U(E)$ on E, equation (10) does not represent a linear eigenvalue problem with respect to the parameter E. Therefore, the operator $P_{\parallel}\overset{1}{H}P+U(E)$ does not represent the inner interaction energy of "the system in the distinguished state" under consideration, as would be the case if $U(E)$ were independent of E and hermitean.

The differential equation

Equation (8) is the integro-differential equation (with respect to time) for the state vector $\Psi_{\parallel}(t)$ of "the system in the distinguished state" under consideration. It may be replaced by an equivalent purely integral equation (with respect to time) by means of an arbitrary Green "function" $G^0(t-t')$ for equation (14). Assuming for simplicity $\Psi_{\perp}(t_0)=0$ and $t_0\to-\infty$, and denoting by $R(t-t')$ the resolving kernel of this integral equation, we can write its solution in the form

$$\Psi_{\parallel}(t)=\Psi^0_{\parallel}(t)-\frac{i}{\hbar}\int_{-\infty}^{\infty}dt'R(t-t')\Psi^0_{\parallel}(t'), \tag{13}$$

where $\Psi^0_{\parallel}(t)$ is an arbitrary state (of "the system in the distinguished state") satisfying the unperturbed equation

$$\left(i\hbar\frac{\partial}{\partial t}-\overset{0}{H}\right)\Psi^0_{\parallel}(t)=0. \tag{14}$$

From (14) it follows that

$$\Psi^0_{\parallel}(t)=e^{-\frac{i}{\hbar}\overset{0}{H}(t-t_0)}\Psi^0_{\parallel}(t_0), \tag{15}$$

where the initial value $\Psi^0_{\parallel}(t_0)$ is an arbitrary state of "the system in the distinguished state". Expressing in (13) $\Psi^0_{\parallel}(t')$ in the integral in terms of $\Psi^0_{\parallel}(t)$, by means of equ. (15), we get

$$\Psi_{\parallel}(t)=(1+A)\Psi^0_{\parallel}(t), \tag{13'}$$

where

$$A=-\frac{i}{\hbar}\int_{-\infty}^{+\infty}dt\,R(t)e^{\frac{i}{\hbar}Ht}. \tag{16}$$

Equation (8) may be reduced to an equivalent purely differential equation with respect to time, if we can find an operator V for which the following equation

$$-\frac{i}{\hbar}\int_{-\infty}^{+\infty} dt' K(t-t')\Psi_{||}(t') = V\Psi_{||}(t) \tag{17}$$

is satisfied identically in the solutions of (8) (cf. [1] and [2]). Introducing (13′) into (17) and remembering that the initial value of the general solution $\Psi^0_{||}$ at an arbitrary but fixed point may be chosen at will, we get the following equation for the operator V

$$V(1+A) = -\frac{i}{\hbar}\int_{-\infty}^{+\infty} dt\, K(t)(1+A)e^{\frac{i}{\hbar}\overset{0}{H}t}.$$

This equation can be solved immediately by multiplying on the right with the operator $(1+A)^{-1}$:

$$V = -\frac{i}{\hbar}\int_{-\infty}^{+\infty} dt\, K(t)(1+A)e^{\frac{i}{\hbar}\overset{0}{H}t}(1+A^{-1}). \tag{18}$$

Conversely, it can easily be shown, that equation (17) is a consequence of (18). We note that, due to the relation $K = P_{||}KP_{||}$, we have $R = P_{||}RP_{||}$, $A = P_{||}AP_{|}$ and $V = P_{||}VP_{||}$.

The above method does not involve expansion in powers of the interaction constant. Assuming that for quantities $\Psi_{||}$ and K such convergent expansions exist

$$K = \sum_{n=2}^{\infty} K^{(n)}, \qquad \Psi_{||} = \sum_{n=0}^{\infty} \Psi^{(n)},$$

and, therefore, also for quantities R and A

$$R = \sum_{n=1}^{\infty} R^{(n)}. \qquad A = \sum_{n=1}^{\infty} A^{(n)},$$

we can calculate from (19)

$$V = \sum_{n=2}^{\infty} V^{(n)}$$

up to an arbitrary order of approximation. E. g. for the first approximation $V^{(2)}$ we get

$$V^{(2)} = -\frac{i}{\hbar}\int_{-\infty}^{+\infty} dt' K^{(2)}(t)\, e^{\frac{i}{\hbar}\overset{0}{H}t}, \tag{19}$$

where

(20) $$K^{(2)}(t)=P_{\parallel}\overset{1}{H}P_{\perp}\theta^{+}(t)e^{-\frac{i}{\hbar}\overset{0}{H}t}P_{\perp}\overset{1}{H}P_{\parallel}.$$

By virtue of (17), we can replace equation (8) in the case of $\Psi_{\perp}(t_0)=0$ and $t_0\to-\infty$ by the equivalent equation

(21) $$\left(i\hbar\frac{\partial}{\partial t}-\overset{0}{H}-P_{\parallel}\overset{1}{H}P_{\parallel}\right)\Psi_{\parallel}(t)=V\Psi_{\parallel}(t)$$

with V given by formula (18). Equation (21) is the purely differential equation (with respect to time) for the state vector $\Psi_{\parallel}(t)$ of "the system in the distinguished state". This equation has the form of a Schrödinger equation with the "potential" $P_{\parallel}\overset{1}{H}P_{\parallel}+V$. In terms of representatives, equation (21) becomes an integral equation with respect to new variables, because operator $P_{\parallel}\overset{1}{H}P_{\parallel}+V$ is an integral operator in any representation. The term V in the "potential" is due to virtual states (i. e. other than the distinguished one) which can exist for the system. It can be shown by examples that operator V is not real (= hermitean): it has both a real part V^R and an imaginary part V^I

$$V=V^R+iV^I.$$

The "potential" $P_{\parallel}\overset{1}{H}P_{\parallel}+V$ is, therefore, complex.

We can go over from (21) to the time-independent equation by means of the substitution

(22) $$\Psi_{\parallel W}(t)=X_{\parallel W}e^{-\frac{i}{\hbar}Wt},\quad \text{thus}\quad \Psi_{\parallel}(t)=\sum_{W}X_{\parallel W}e^{-\frac{i}{\hbar}Wt}b_W,$$

where

(23) $$W=\bar{E}_{\parallel}-i\Gamma$$

is a complex number (note that the expansion in (22) is not orthogonal). In this way we get equation

(24) $$(W-\overset{0}{H}-P_{\parallel}\overset{1}{H}P_{\parallel})X_{\parallel W}=VX_{\parallel W}.$$

The real number $\bar{E}_{\parallel}$ may, according to (22) and (23), have the meaning of the expectation value in the state $X_{\parallel W}$ of "the energy of the system in the distinguished state" (not of the total energy of the system $\overset{0}{H}+\overset{1}{H}$). The real number $\Gamma/\hbar$ may be considered as the probability of the transition from the state $X_{\parallel W}$ to all other states per unit time. The number $\tau=\hbar/\Gamma$ is, therefore, the life-time of the state $X_{\parallel W}$.

Assuming the normalization condition for $X_{\parallel W}$ to be

$$\langle X_{\parallel W}X_{\parallel W}\rangle=1$$

we get from (24), due to the hermitean character of the operators $\overset{0}{H}+P_{||}\overset{1}{H}P_{||}+V^R$ and V^I,

$$\bar{E}_{||}=\langle X_{||W}(\overset{0}{H}+P_{||}\overset{1}{H}P_{||}+V^R)X_{||W}\rangle \tag{25}$$

and

$$\Gamma=\langle X_{||W}V^I X_{||W}\rangle . \tag{26}$$

It ought to be emphasized, however, that the $X_{||W}$ are not simultaneous eigenstates of the operators $\overset{0}{H}+P_{||}\overset{1}{H}P_{||}+V^R$ and V^I, since these operators do not commute with each other.

The operator $\overset{0}{H}+P_{||}\overset{1}{H}P_{||}+V^R$ commutes with the operator $P_{||}$, owing to the property $V^R=P_{||}V^RP_{||}$ (by which it differs from operator $\overset{0}{H}+\overset{1}{H}$). This fact, together with formula (25), suggests that $H_{||}=\overset{0}{H}+P_{||}\overset{1}{H}P_{||}+V^R$ may be considered as the proper operator representing "the energy of the system in the distinguished state" (the total energy of the system being $H=\overset{0}{H}+\overset{1}{H}$).

Equation (24) is neither an eigenvalue problem for the total energy of the system (in contradistinction to (12)) nor the eigenvalue problem for "the energy of the system in the distinguished state". It also differs from the equation (10) for the distinguished component $\Phi_{||E}$ of an eigenstate Φ_E of the total energy of the system. The state $X_{||W}$ becomes an eigenstate of "the energy of the system in the distinguished state", and at the same time – of the total energy of the system, if $V^IX_{||W}=0$. In this case $X_{||W}=\Phi_{||E}$. We call $X_{||W}$ the quasi-stationary state of "the system in the distinguished state". The quasi-stationary state $X_{||W}$ is stabile, i. e. becomes stationary, if $V^IX_{||W}=0$.

In the first example given in the Introduction, $P_{||}\overset{1}{H}P_{||}=0$, thus the "potential" is represented by operator V. The operator $H_{||}=\overset{0}{H}+V^R$ is here the energy of N_0 particles, the operator V^I describes the transition of the system from the state corresponding to N_0 particles to all other states. A discussion of this instance will be published elsewhere.

In the second example the operator $H_{||}=\overset{0}{H}+P_{||}\overset{1}{H}P_{||}+V^R$ is the energy of the scatterer in state $|a_0\rangle$ and the particle; the operator V^I describes the transition of the system from the state corresponding to the scatterer in state $|a_0\rangle$ and to the particle to all other states.

For consideration of the second instance the representation given by the base vectors $|\lambda(1)a\rangle=|\vec{p}a\rangle$ should be used, where $\lambda(1)=\vec{p}$ is a momentum eigenvalue of the particle. Assuming that there is no external interaction on the system, we have

$$\overset{0}{H}|\vec{p}a\rangle=E_{\vec{p}a}|\vec{p}a\rangle .$$

Equations (21) and (24) expressed in this representation take, respectively, the forms:

$$\left(i\hbar\frac{\partial}{\partial t}-E_{\vec{p}a}\right)\Psi(\vec{p}a_0,t)=\int d_3p'\langle\vec{p}a_0|\overset{1}{H}+V|\vec{p}'a_0\rangle\Psi(\vec{p}'a_0,t), \tag{27}$$

where

$$\Psi(\vec{p}a_0,t)=\langle\vec{p}a_0|\Psi_{||}(t)\rangle=\langle\vec{p}a_0|\Psi(t)\rangle,$$

and

$$(W-E_{\vec{p}a_0})X_W(\vec{p}a_0)=\int d_3p'\langle\vec{p}a_0|\overset{1}{H}+V|\vec{p}'a_0\rangle X_w(\vec{p}a_0), \tag{28}$$

where $X_W(\vec{p}a_0)=\langle\vec{p}a_0|X_{||W}\rangle$. Replacing the operator V by its lowest approximation $V^{(2)}$ given by (19) and (20), we obtain the following formula for the non-zero matrix elements of the "potential" $P_{||}\overset{1}{H}P_{||}+V$:

$$\langle\vec{p}a_0|\overset{1}{H}+V^{(2)}|\vec{p}a'_0\rangle=\langle\vec{p}a_0|\overset{1}{H}+U^{(2)}(E_{\vec{p}'a_0})|\vec{p}'a_0\rangle= \tag{29}$$

$$=\langle\vec{p}a_0|H|\vec{p}'a_0\rangle+P\int d_3p''\sum_{a''\neq a_0}\frac{\langle\vec{p}a_0|\overset{1}{H}|\vec{p}''a''\rangle\langle\vec{p}''a''|\overset{1}{H}|\vec{p}'a_0\rangle}{E_{\vec{p}'a_0}-E_{\vec{p}''a''}}-$$

$$-i\pi\int d_3p''\sum_{a''\neq a_0}\langle\vec{p}a_0|\overset{1}{H}|\vec{p}''a''\rangle\langle\vec{p}''a''|\overset{1}{H}|\vec{p}'a_0\rangle\,\delta(E_{\vec{p}'a_0}-E_{\vec{p}''a''}).$$

It can be seen from this approximation that the "potential" $P_{||}\overset{1}{H}P_{||}+V$ is in general a complex operator.

To equation (28) may be applied the stationary perturbation method. Using the "potential" $P_{||}\overset{1}{H}P_{||}+V^{(2)}$ and treating it as a perturbation, we get for Γ in the first order approximation an expression of the Weisskopf-Wigner type (cf. e. g. [3]). Indeed, we get

$$W=E_{\vec{p}a_0}+\langle\vec{p}a_0|H+V^{(2)}|\vec{p}'a_0\rangle,$$

where the correction $\langle\vec{p}a_0|\overset{1}{H}+V^{(2)}|\vec{p}a_0\rangle$ is given by formula (29) with $\vec{p}'=\vec{p}$. Comparison with (23) yields for Γ the expression

$$\Gamma=\pi\int d_3p'\sum_{a'\neq a_0}|\langle\vec{p}a_0|\overset{1}{H}|\vec{p}'a'\rangle|^2\,\delta(E_{\vec{p}a_0}-E_{\vec{p}'a'}).$$

In the above instance the complex "potential" $P_{||}\overset{1}{H}P_{||}+V$ becomes, after an approximating and averaging procedure, a complex potential of the Feshbach-Porter-Weisskopf type (cf. [4] and [5]).

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THEORETICAL PHYSICS

On the Variational Principle of Dielectrics

by

G. MARX

Presented by L. INFELD on November 23, 1955

Since the foundation of the theory of relativity the variational principle both of hydrodynamics and phenomenological electrodynamics has been dealt with many times. The investigations, however, were not free from complications in either of these fields [1]. The purpose of the present note is to show that by choosing for the Lagrangian the simplest possible invariants of the problem the variational principle leading to the correct equations of motion can be directly obtained. The results of the present note do not differ fundamentally from those quoted in the literature; they point out, however, the great usefulness of the variational principle, because of its simplicity, in promoting investigations in different fields: e. g. the investigation of the energy-monumentum-conditions in phenomenological electrodynamics.

Let us first consider the case of an ideal fluid. For the description of the motion of the fluid we use the four-velocity u^i, which is identical with the unity vector determining the direction of flow in four-space:

$$u_i u^i \equiv g_{ik} u^i u^k = -c^2. \tag{1}$$

The distribution in space of the rest mass is described by the rest mass density μ. The relation between μ and the total rest mass M in a given volume is *)

$$M = \int_V \mu dV_0. \tag{2}$$

dV_0 is the volume of a volume element measured in the instantaneous geodetic system, which is related to the proper time τ of the matter and

*) This is essentially the same as the Weyl definition [2]:

$$\int\int dM\, d\tau = \frac{1}{c}\int \mu \sqrt{g}\, dx.$$

the co-ordinate differentials of its volume in the following manner

$$\sqrt{g}\,dx = dV_0 c\,d\tau, \quad \text{i. e.} \quad dV_0 = \sqrt{g}\,\frac{dt}{d\tau}\,dV, \tag{3}$$
$$\text{where} \quad i\,dx = dV\,dx^4 = dx^1 dx^2 dx^3 dx^4.$$

In the ideal fluid there are no stresses operative, only an isotropic pressure, which can be described by the scalar function p. Our first task is to formulate the variational principle of the motion of an ideal fluid. The simplest invariant having the character of energy-density, which can be set up from the quantities available, is

$$L = \mu c^2 - p. \tag{4}$$

Let us choose this for our Lagrangian. The energy-momentum-tensor can be obtained from the integral

$$S = \int L \sqrt{g}\,dx \tag{5}$$

by varying g_{ik}. In carrying out the variation one must take into account that the rest mass M (in an arbitrary volume) as well as the pressure p are of course independent of g_{ik}. In the equation

$$M = \int_V \mu \frac{dt}{d\tau} \sqrt{g}\,dV, \tag{6}$$

defining the mass density, g_{ik} is already involved; thus μ cannot be regarded as independent of g_{ik}. According to definition

$$\frac{dt}{d\tau} = \frac{c}{\sqrt{-g_{ik} v^i v^k}}, \qquad \text{where} \qquad v^k = \frac{dx^k}{dt}\ (v^4 = ic), \tag{7}$$

v^i is the quotient of co-ordinate differentials. Thus from the variational point of view v^i can be regarded as independent from g_{ik}. Let us vary in the identity (6) g_{ik} and take into account (7). We get

$$0 = \int_V \left[\frac{\partial \mu}{\partial g_{ik}} - \frac{1}{2}\mu\left(g_{ik} + \frac{1}{c^2} u_i u_k\right)\right] \frac{dt}{d\tau} \sqrt{g}\,\delta g^{ik}\,dV. \tag{8}$$

Here we have used

$$u^r = v^r \frac{dt}{d\tau} = \frac{v^r c}{\sqrt{-g_{ik} v^i v^k}}. \tag{9}$$

In the case of arbitrary δg^{ik} and v^i, (8) is satisfied and thus equation (6) is an identity (and not a restrictive auxiliary condition) only if

$$\frac{\partial \mu}{\partial g^{ik}} = \frac{1}{2}\mu\left(g_{ik} + \frac{1}{c^2} u_i u_k\right). \tag{10}$$

Knowing this and with the help of (5) we may express the energy-momentum-tensor of an ideal fluid according to the relation

$$\delta S = \frac{1}{2}\int T_{ik}\sqrt{g}\,\delta g^{ik}dx. \tag{11}$$

We immediately obtain

$$T_{ik} = \mu u_i u_k + p g_{ik}. \tag{12}$$

Let us now pass over to the case $g_{ik} = \delta_{ik}$. From the derivation of (11) it follows directly that

$$\partial_k T_{ik} = 0. \tag{13}$$

Expanding this we get

$$\mu u_k \partial_k u_i + u_i \partial_k(\mu u_k) + \partial_i p = 0. \tag{14}$$

Multiplying by u_i and taking into account (1), we obtain the following relation:

$$\partial_k(\mu u_k) = \frac{1}{c^2} u_k \partial_k p. \tag{15}$$

It is evident that a rest mass M in a fixed volume element which can be obtained from (2), is not constant even if on the boundary surface we have $u_k = 0$ (this means that there is no mass outflow). This can be attributed to the fact that the force due to the pressure is not perpendicular to the world lines of the flow, and thus it may cause a change in the rest mass [3]. (The essential part of this conception also occurs in the work of Takabayashi [4]).

If we wish to introduce, instead of μ, a mass density μ_0 for which the continuity equation

$$\partial_k(\mu_0 u_k) = 0$$

holds, i. e. from which a constant M_0 mass can be derived, we can write

$$\mu = \mu_0\left(1 + \frac{P}{c^2}\right). \tag{16}$$

With regard to (15) this can be attained if the relation

$$\partial_i p = \mu_0 \partial_i P, \quad \text{i. e.} \quad P = \int \frac{dp}{\mu_0} \tag{17}$$

exists. P is the well known pressure potential of hydrodynamics, with the aid of which the equation of motion can be transformed into the following form:

$$u_k \partial_k \left[\left(1 + \frac{P}{c^2}\right)u_i\right] \equiv \frac{d}{d\tau}\left[\left(1 + \frac{P}{c^2}\right)u_i\right] = -\partial_i P. \tag{18}$$

This relativistic equation of motion of the ideal fluid was set up by several authors, first of all by Lamla [5]. It is remarkable that the form (18) perfectly agrees with the equation of motion in a scalar field [4]. This means that the simple method first proposed for the treatment of relativistic motion in a scalar field by Werle [6], [4] can also be applied to the flow of an ideal fluid. The method may be of significance in the hydrodynamic theory of nuclear reactions.

Let us now consider the case when the continuous medium is charged and generates an electromagnetic field, which may, in turn, polarise the medium. (For simplicity we disregard the case of magnetic polarisability. It is evident, however, that the calculation can easily be generalised to this case too). Let the dielectric coefficient of the medium be denoted by ε. According to phenomenological electrodynamics the field can be described by two tensors [1], [7]:

$$(19) \quad F_{ik}=\nabla_i\varphi_k-\nabla_k\varphi_i, \qquad H_{ik}=F_{ik}-\frac{\varepsilon-1}{c^2}(F_i u_k-F_k u_i), \quad \text{where} \quad F_i=F_{ik}u^k.$$

The simplest Lagrangian possible, describing the motion of the medium (for simplicity assumed to be an ideal fluid), the electromagnetic field and the interaction of both of these, is

$$(20) \qquad L=\mu c^2-p+\frac{1}{4}F_{rs}H^{rs}-\varphi_r j^r, \qquad j^r=\frac{1}{c}\varrho_0 u^r.$$

Here ϱ_0 is the rest charge density interpreted by the equation

$$(21) \qquad e=\int\limits_V \varrho_0\, dV_0=\frac{1}{c}\int\limits_V \varrho_0\frac{dt}{d\tau}\sqrt{g}\, dV.$$

The variation of the integral of L with respect to the vector potential φ leads to the Maxwell-Minkowski field equations

$$(22) \qquad \nabla_k H^{ik}=j^i.$$

From the variational integral the common energy-momentum-tensor of the medium and the electromagnetic field can also be obtained according to (11). In carrying out the variation it must be taken into account that φ_i and p are independent of g^{ik}, but the mass density is not as the equation defining it involves g^{ik}. The dependence of μ is determined by (10). The same is valid for the charge density ϱ_0 determined by (21). Thus

$$(23) \qquad \frac{\partial\varrho_0}{\partial g^{ik}}=\frac{1}{2}\varrho_0\left(g_{ik}+\frac{1}{c^2}u_i u_k\right).$$

g_{ik} is also involved in the four-velocity vector u^r as the identity (1) must be valid for any choice of g_{ik}. From (9) it is evident that

$$(24) \qquad \frac{\partial u^r}{\partial g^{ik}}=-\frac{1}{2c^2}u^r u_i u_k.$$

Finally we must assume that the polarisability of the medium depends on its density $\varepsilon = \varepsilon(\mu)$; owing to this

$$\frac{\partial \varepsilon}{\partial g^{ik}} = \frac{d\varepsilon}{d\mu} \cdot \frac{\partial u}{\partial g^{ik}} = \frac{1}{2} \mu \frac{d\varepsilon}{d\mu} \left(g_{ik} + \frac{1}{c^2} u_i u_k \right). \tag{25}$$

Taking all this into account the Lagrangian (20) can easily be varied with respect to g_{ik}. With the help of (11) the following energy-momentum-tensor is obtained

$$T_{ik} = \mu u_i u_k + p g_{ik} + \theta_{ik}, \tag{26}$$

where

$$\theta_{ik} = \left(F_{ir} F^r_k - \frac{g_{ik}}{4} F_{rs} F^{rs} \right) - \frac{\varepsilon - 1}{c^2} \left(F_i F_k - \frac{g_{ik}}{2} F_r F^r - \frac{1}{c^2} u_i u_k F_r F^r \right) - \frac{F_r F^r}{2c^2} \mu \frac{d\varepsilon}{d\mu} \left(g_{ik} + \frac{1}{c^2} u_i u_k \right). \tag{27}$$

The expression (27) is the energy-momentum-tensor of the electromagnetic field. Except for its last term it agrees perfectly with the energy-momentum-tensor of Abraham, first deduced by Novobátzky [7] from a Lagrangian slightly different from the one used here:

$$\theta^A_{ik} = \left(F_{ir} F^r_k - \frac{g_{ik}}{4} F_{rs} F^{rs} \right) - \frac{\varepsilon - 1}{c^2} \left(F_i F_k - \frac{g_{ik}}{2} F_r F^r - \frac{1}{c^2} u_i u_k F_r F^r \right). \tag{28}$$

The last term in (27) refers to the electrostriction and thus θ_{ik} can be regarded as the natural co-variant generalisation of the expression (28) proposed by Abraham. (The non-covariantly completed expression in the case of a resting dielectric with electrostriction can be found among others in [8]).

We now pass over to the case of an incompressible fluid. We may write $P = p/\mu_0$ and thus

$$T_{ik} = \mu_0 u_i u_k + p \left(g_{ik} + \frac{1}{c^2} u_i u_k \right) + \theta_{ik}, \tag{29}$$

where

$$\theta_{ik} = \theta^E_{ik} + p^* \left(g_{ik} + \frac{1}{c^2} u_i u_k \right). \tag{30}$$

p^* in the energy-momentum-tensor θ_{ik} of the electromagnetic field denotes the following:

$$p^* = \frac{1}{2c^2} F_r F^r \left(1 - \mu \frac{d}{d\mu} \right) (\varepsilon - 1). \tag{31}$$

It can be seen that in addition to the expression

$$\theta^E_{ik} = \left(F_{ir} F^r_k - \frac{g_{ik}}{4} F_{rs} F^{rs} \right) - \frac{\varepsilon - 1}{c^2} \left(F_i F_k - \frac{1}{2c^2} u_i u_k F_r F^r \right) \tag{32}$$

the tensor θ_{ik} involves a term proportional to p^*, the form of which perfectly agrees with that part of the energy-momentum-tensor of the fluid which refers to the hydrostatic pressure. Thus p^* refers to the pressure-like isotropic force exerted by the electromagnetic field (polarisation pressure). In the simplest case when the complete dipole momentum produced by the given field strength F_{ik} is independent of the volume of the matter, i. e. the susceptibility $(\varepsilon-1)$ is proportional to the density μ, according to (28) equals zero. This term plays no important role, anyway, as both the integral force and the torque exerted by it are equal to zero. The effect of p^* consists altogether in causing hydrostatic pressure in the interior of the medium. (This was pointed out in electrostatics by Györgyi [4]). The complete energy-momentum-tensor can also be written in the form

$$T_{ik}=\mu_0 u_i u_k+(p+p^*)\left(g_{ik}+\frac{1}{c^2}u_i u_k\right)+\theta^E_{ik}. \tag{33}$$

If the term p^* is neglected (either because of the proportionality of $\varepsilon-1$ to μ or because of its fusion into p) we obtain from (32) the energy-momentum-tensor of the electromagnetic field. This is equivalent to the tensor set up for a resting medium by Einstein and Laub [10]. With the aid of thermodynamical considerations, Kluitenberg also obtained an energy-momentum-tensor not fundamentally different from (32) [11].

$$\theta^k_{ik}=\left(F_{ir}F^r_k-\frac{g_{ik}}{4}F_{rs}F^{rs}\right)-\frac{\varepsilon-1}{c^2}\left(F_iF_k-\frac{1}{c^2}u_i u_k F_r F^r\right). \tag{34}$$

As Kluitenberg has pointed out, the discrepancy in the last term can be explained by the fact that he substitutes the mass density μ_0 in the kinetic energy-momentum-tensor by another expression μ_0', where $\mu_0'-\mu_0=-\frac{\varepsilon-1}{2c^2}F_rF^r$ mass equivalent of the polarisation energy; thus finally T_{ik} is equal to the expression

$$T_{ik}=\left(\mu_0-\frac{\varepsilon-1}{2c^2}F_rF^r+\frac{p+p^*}{c^2}\right)u_i u_k+(p+p^*)g_{ik}+\theta^k_{ik}.$$

From what has been said so far it is evident that there is no fundamental difference between the Abraham (28) the Einstein-Laub (32) and the Kluitenberg tensors (34), all three can be regarded as special cases of the tensor in (26) and (27) involving electrostriction *). We may thus repeat the statement emphasized by Novobátzky [7] that the application of the variational principle makes it possible to solve the energy-

*) Abraham's tensor is an advance with respect to others, in that its spur is zero, as is the case for the electromagnetic energy-momentum-tensor of vacuum; thus, it gives a vanishing rest mass density for the field.

momentum-problem of the phenomenological electrodynamics in an unambiguous manner, free from arbitrary assumptions.

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CHEMISTRY

The Influence of Polar Organic Substances and Catalytic Poisons on Hydrogen Overvoltage on Nickel and Iron Cathodes

by
W. PALCZEWSKA

Presented by M. ŚMIAŁOWSKI on September 21, 1955

During an investigation of the expansion of spiral iron cathodes caused by the penetration of hydrogen, Śmiałowski and Szklarska-Śmiałowska [1] established that this phenomenon — quite distinct, for instance, in a solution of sulphuric acid containing also arsenious acid — diminishes when the solution contains also dibenzylsulphoxide and, finally, stops altogether when the concentration of the sulphoxide exceeds 30 mg./l.

The expansion of the iron cathode observed in an electrolyte containing arsenious acid was attributed to the increasing concentration of atomic hydrogen evolved during electrolysis on the surface of the cathode, and the consequent more intensive penetration of the hydrogen into the material of the cathode. Arsenic acted in these solutions as an inhibitor impeding the process of hydrogen combination. When the sulphuric acid solution contained no arsenic, the cathode failed to expand. The role of the sulphoxide which suppressed the influence of arsenic called for an explanation.

With this object in view, an examination was made of the shape of polarisation curves for nickel and iron cathodes in aqueous sulphuric acid solutions containing arsenious acid and dibenzylsulphoxide.

The cathodes were made of nickel and iron wire; in the latter instance, carbonyl-iron, containing 0.03 per cent of carbon was used. The diameter of the wire was 0.5 mm., the surface about 0.5 sq. cm. A platinum plate served as an anode.

An "H"-shaped vessel was used for electrolysis of the solution investigated. The anodic and cathodic compartments were separated by a thick layer of glass wool.

In the course of the experiments, the cathodic compartment was continuously supplied with hydrogen.

The arrangement used in the researches in question was analogical to that used in similar experiments.

The potential of the cathode examined was measured against an Hg Hg_2SO_4/1N H_2SO_4 electrode. The electromotive force was measured with the aid of a compensator, permitting exact readings down to 0.1 mV, and a galvanometer of a 10^{-8} A sensitivity.

Polarising the cathode, a current density of 10^{-3} A/cm². was applied and raised by steps, whenever the electromotive force became suffi-

Fig. 1

– – – – – – – – solutions containing As

△ 1N H_2SO_4+$(C_6H_5CH_2)_2SO$ [30 mg./l.]

○ 1N H_2SO_4+$(C_6H_5CH_2)_2SO$ [100 mg./l.]

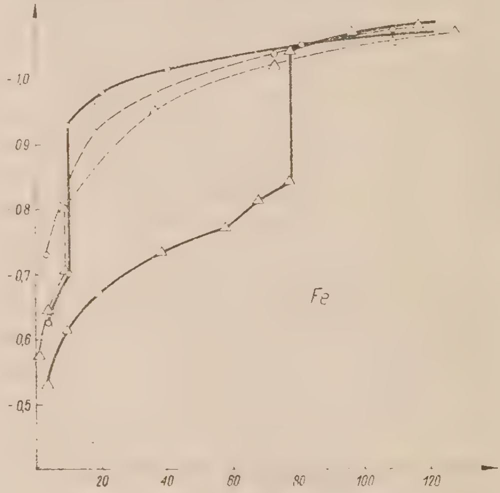

Fig. 2

– – – – – – – – solutions containing As

△ 1N H_2SO_4+$(C_6H_5CH_2)_2SO$ [20 mg./l.]

○ 1N H_2SO_4+$(C_6H_5CH_2)_2SO$ [50 mg./l.]

ciently stabilised, up to the final value of 10^{-1} A/cm². The readings were taken at a temperature of 18 ± 3^0 C., and expressed in the hydrogen scale.

The following solutions were examined:

1) 1N H_2SO_4;

2) 1N H_2SO_4 containing 100 mg./l. of dissolved As_2O_3;

3) 1N H_2SO_4 containing dibenzylsulphoxide in quantities of 2 to 100 mg./l.;

4) 1N H_2SO_4 containing various quantities of dibenzyl sulphoxide (p. 3) and 100 mg./l. of As_2O_3.

The curves shown in Figs. 1 and 2 illustrate the results for nickel and iron cathodes respectively; they express the dependence of the cathodic potential values (on the hydrogen scale) on the density of the cathodic current for solutions of different compositions.

The results of readings proved to be reproducible to an accuracy of 50 mV. Owing to this poor reproducibility, the values obtained in this work are subject to considerable error. Accurate determination was

not the object of this work. The character of the resulting curves, however, is of great significance. It indicates the possibility of explaining the failure of iron cathodes to expand in solutions of sulphuric acid containing arsenious acid and dibenzylsulphoxide.

Dibenzylsulphoxide, added to a solution of sulphuric acid, raises the hydrogen overvoltage. When sufficient quantities of sulphoxide are added to the solution (30 and 20 mg. in the cases of nickel and iron respectively), the polarisation curves take on a characteristic shape. They are composed of three sections:

I — is obtained when current densities are low; it shows little differences in the overvoltage resulting from the changing concentrations of the sulphoxide in the solution;

II — represents a leap of about 200 mV in the hydrogen overvoltage, which begins at the cathodic potential of −650 to −750 mV for nickel, and −700 to −800 mV for iron;

III — runs an even course (within the limits of experimental error) at 20 to 100 mg./l. concentrations of the sulphoxide.

Observations have shown that characteristic changes in the picture presented by the bubbles of hydrogen evolving on the cathode correspond to this shape of curve.

I — Hydrogen bubbles of various sizes appear on the cathode, the spots at which they leave it being scattered at random.

II — With the rise of the cathodic potential represented by the leap of the polarisation curve, the diameter of the bubbles increases to 3 mm. Then they travel vertically upwards, leaving the cathode at the upper end. This is a characteristic picture of the cathode on which hydrogen is evolved from an acid solution containing dibenzylsulphoxide [2].

III — The picture of the cathode does not undergo further changes.

The first and third sections of the curve are in general agreement with Tafel's equation.

When the solution examined contained also arsenious acid in addition to at least 20—30 mg./l. of dibenzyl sulphoxide, the character of the polarisation curves did not alter. The only change was observed in the value of the cathodic potential at which the polarisation curve showed a sudden leap; it was shifted towards more positive values. The characteristic threshold value of the potential was about −600 mV for nickel and about −700 mV for iron. In the case of solutions containing sufficiently large amounts of sulphoxide, the leap of the potential of the electrode appeared at such low current densities that actual experimental conditions made observations impossible.

In solutions containing arsenious acid, the changes in the picture presented by the hydrogen bubbles correspond to the particular sections of the polarisation curve in the same manner as before.

In a molecule of dibenzylsulphoxide, the bond between sulphur and oxygen is polarised. Near the cathode, the sulphur atom — being more positive — is orientated towards the surface of the cathode, while the benzyl groups and the oxygen are orientated towards the bulk of the solution. If the adsorption of sulphoxide appears, the surface of the cathode becomes hydrophobic, the interfacial surface tension between the electrode, solution and gas alters, and, consequently, there is also a change in the size and the shape of the bubbles of hydrogen evolved on the cathode.

As has been shown in this paper, the sulphoxide produces a characteristic change in the appearance of the bubbles of gas evolving on the electrode only after the cathodic potential exceeds the threshold value observed. This may suggest the conclusion that the sulphoxide is then absorbed on the surface of the electrode and covers the latter with a monomolecular layer. The course of the polarisation curves, beyond the leap of the potential, indicates that the electrode is covered with sulphoxide to a maximum already at 20—30 mg./l. concentrations of the latter substance (in the case of electrodes with an 0.5 sq. cm. surface, and 40 ml. of catalyte), since a further rise in the concentration of the substance in the solution fails materially to affect the track of the third section of the polarisation curve.

The adsorption of ions and electrically neutral molecules on polarised cathodes has in recent years been the subject of numerous investigations. It has been established that adsorption and desorption on the electrode is expressed by the characteristic flexions of Tafel's line and by changes of the electrocapillary curve and capacity of the double layer [3]. On the basis of results obtained, it has been established that the adsorption of the molecules takes place near the zero-point of the electrode metal.

The principal basic research in this domain was conducted by Frumkin, Iofa and Kabanov, and, more recently, by Nikolaieva, Frumkin, Iofa (adsorption on mercury) [4], Bune, Kolotyrkin (adsorption of anions on lead) [5], Loshkariev and Kriukova [6], and Kolotyrkin and Miedviedieva [7].

Data relating to the zero-point of the charge for nickel as well as for iron are contradictory and open to serious doubt. In the case of nickel, the value of 0 volts on the hydrogen scale, is sometimes quoted. The results obtained in the course of this research demonstrate that the value for nickel, as well as for iron, should lie rather near —0.7 V since adsorption of the sulphoxide starts at a point somewhere near this value. Other experimental methods are necessary in order to determine whether the zero-point of nickel or iron has in fact such a negative potential.

The mechanism by which the hydronium ion is discharged on the cathode covered with a layer of an adsorbed, surface-active substance

is not yet fully explained. Thin layers of such substances cause a rise of the overvoltage. It is assumed that such a layer screens the surface of the electrode, repels the ions of the double layer into the electrolyte and decreases the effect of the electric field on the activation energy of the ions.

It was established during this research that arsenious acid facilitates sulphoxide adsorption and causes it to take place at a more positive cathodic potential. First, the electrode is covered with arsenic, and then — at a different potential — the adsorption of sulphoxide takes place. The shape of the polarisation curve within the zone of section III, as well as all other corresponding observations, fail to reveal any substantial difference as compared to the results obtained with solutions containing no arsenic, since, eventually, a layer of sulphoxide has formed at the interface between the electrode and the solution. Consequently, in the presence of sufficient amounts of sulphoxide, arsenic should have no influence on the expansion of the cathode. This is in agreement with the observations of Śmiałowski and Szklarska-Śmiałowska. The sulphoxide screens the surface of the cathode, thus preventing a rise in the concentration of the atomic hydrogen; probably, this hydrogen is chiefly removed on the pathway of the following reaction:

$$H + H_3O^+ + e^- = H_2 + H_2O,$$

which may play a considerable role when the electrode is substantially covered with the substance adsorbed.

Conclusions

On the basis of the shape of the polarisation curves and observations of hydrogen bubbles evolving on iron and nickel cathodes, it has been established that in 1N H_2SO_4 containing 20—30 mg./l. (or more) of dibenzylsulphoxide, the latter substance is adsorbed: on nickel at a cathodic potential of -0.65 V to -0.75 V, and on iron at -0.7 V to -0.8 V. In 1N H_2SO_4 containing arsenious acid in addition to the quantity of sulphoxide mentioned above, the latter adsorbs on nickel and iron cathodes at the potentials of -0.6 V and -0.7 V respectively. The values of the potential at which dibenzylsulphoxide is adsorbed on nickel or iron cathodes, justify the suggestion that the potential of the zero-charge of these metals lies near -0.7 V.

Beginning with 30 mg./l. and 20 mg./l. sulphoxide concentrations for nickel and iron cathodes respectively, the electrode becomes covered with sulphoxide to a maximum degree when the adsorption potential is exceeded. The monomolecular layer of sulphoxide checks the effect of arsenic evolved on the cathode in solutions containing arsenious acid. The concentration of atomic hydrogen on the cathode is reduced owing

to the adsorption of dibenzylsulphoxide. This accounts for the failure of iron cathodes to expand, observed by Śmiałowski and Szklarska-Śmiałowska in sulphuric acid solutions containing also suitable amounts of dibenzylsulphoxide, in addition to arsenious acid.

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CHEMISTRY

Is There a Quantitative Relationship Between Hydrogen Overvoltage and the Solubility of This Gas in Metals?

by

M. ŚMIAŁOWSKI

Presented on November 15, 1955

Years ago Nernst [1] put forward the assumption that, during electrolysis, hydrogen only forms bubbles when a sufficient quantity of gas has been occluded by the cathode. This being so, it follows that there must be a quantitative relationship between the ability of a given metal to occlude hydrogen and the value of the overvoltage on that metal.

Thiel and Hammerschmidt [2] contested the correctness of this view. In a more recent work, Kazinczy [3] likewise found no connection between the hydrogen overvoltage and the rate of flow of this gas through an iron cathode.

In earlier papers [4] we showed that iron samples expand under the influence of cathodic polarisation in acids which contain such catalytic poisons as P, As, Sb, S, Se and Te.

Measurements made on soft iron rods acting as cathodes during electrolysis of sulphuric acid, to which arsenic trioxide had been added, enabled Krupkowski and the author of this paper [5] to estimate approximately the pressure created by hydrogen which penetrates into the bulk of the metal cathode. The most probable value of this pressure lies between 10^5 and 10^7 atmospheres. This seems, provided Ubbelohde's assumption is correct, to correspond to the "metallic" form of hydrogen.

In a paper written by the author in collaboration with Foryst [7] it was stated that there is less plastic deformation of cathodes in the case of deoxidised iron samples than in the case of those which are not deoxidised and which, consequently, contain more impurities and non-metallic inclusions. Torsion tests, on the other hand, did not reveal in these two types of iron any differences as regards brittleness caused by cathodic hydrogen.

In a paper written in collaboration with Szklarska-Śmiałowska [8] it was shown that nickel does not expand under the influence of cathodic

polarisation but becomes brittle. This brittleness evidently corresponds to an earlier stage of hydrogenation than plastic deformation.

The above results, together with Kozłowski's observations [9] concerning changes in magnetic coercivity, Palczewska's measurements [10] in connection with the relation between the potential of iron and nickel and the current density, and also measurements made by Szklarska-Śmiałowska [11] to determine to what extent the respective potentials of polarised iron, nickel and copper are dependent on time, lead us to the conclusion that hydrogen in the first stage penetrates into the polarised cathode in the ionic form, creating probably an "intermetallic" compound MH_x, which only after a certain stage of saturation has been reached dissociates, giving atomic hydrogen:

$$MH_x \rightarrow M + xH$$

which, in turn, forms on the surfaces of the crystals molecular hydrogen in the reaction $2H \rightarrow H_2$. If this reaction occurs on the external surface of the crystal then the molecular hydrogen escapes into the atmosphere. But if it develops on the internal surface, in a place from which the molecular hydrogen is unable to escape, a blister is formed, in which the pressure continues to rise until the metal wall cracks, or until diffusion of atomic hydrogen in the opposite direction begins; namely, the partial pressure of atomic hydrogen in mixture with molecular according to the reaction

$$2H \rightleftarrows H_2$$

is directly proportional to the square root of the total pressure.

It is worthy of note that the possibility of protons penetrating into the cathode during electrolysis of an acid has recently been considered by various authors, among them, for example Sutra [12]. On the other hand, papers published by Sarry [13] point to the probable existence of unstable compounds such as FeH_2, FeH_6 or NiH_2.

Acceptance of this theory of the penetration of hydrogen into the metal makes it possible to explain the different values of hydrogen overvoltage observed on different metals in a way other than that proposed by Frumkin [14], Bockris [15], and others.

Let us assume that during electrolysis of an acid some of the total number of hydrogen ions reaching the surface of the cathode, after dehydration, penetrate into the metal. Depending on the absorption capacity of the metal cathode, this process of charging the metal cathode with protons is sooner or later checked. When a certain stage of saturation has been reached in the surface layer of the metal, the protons tend to escape from it; some of them discharge within the metal crystals and on the grain boundaries, or on other defects in the crystalline structure of the metal and produce blisters filled with molecular hydrogen. The

majority, however, begin to escape outwards and in the first stage create adsorbed atoms on the surface. These recombine afterwards into molecules and escape into the atmosphere. The state of saturation of the metal with protons is thus disturbed and so still more of the latter are able to leave the electrolyte.

If we accept the possibility of the above cycle of phenomena, at least in the case of some metals, we are then in a position to state that two mechanisms are admissible — mechanism *A*, which characterises metals with a high hydrogen overvoltage, such as mercury or lead which probably dissolve only insignificant quantities of hydrogen, (according to Frumkin [14] the factor determining the value of the hydrogen overvoltage on these metals is the slow rate at which the hydrogen ions are discharged), and mechanism *B*, which provides a second means of escape for the hydrogen ions and thus lowers the overvoltage value.

Mechanism *A*:

(1) Discharge of hydrogen ions

$$(H_3O)^+ + e^- + M \rightarrow MH$$

(2) Desorption — either catalytic

$$MH + MH \rightarrow 2M + H_2$$

or electrochemical

$$(H_3O)^+ + MH + e^- \rightarrow M + H_2$$

Mechanism *B*:

(1) Penetration of protons into the cathode

$$x(H_3O)^+ + xe^- + M \rightarrow [M(H^+e^-)_x] \quad \text{(solid solution } MH_x \text{ in M)}$$

(2) Escape of hydrogen from interior of the metal to the surface

$$[M(H^+e^-)_x] \rightarrow MH$$

(3) Desorption — like 2 in mechanism *A*.

According to this conception, on metals incapable — or almost incapable — of dissolving protons, process *A* would take place — i. e. direct discharge of hydrogen ions on the surface of the cathode, and the creation — in the well-known cycle of changes — of molecular hydrogen. Observation has shown that the principal factor determining the overvoltage value is, in this case, the rate of discharge of hydrogen ions.

On the other hand, on metals capable of dissolving protons both process *A* and process *B* would be expected to take place. The latter process involves the dissolution of protons which in turn give atoms and molecules in the familiar cycle of secondary reactions. Process *B* aids process *A* and thus lowers the overvoltage. In all probability, how-

ever, the factor determining the overvoltage value is not only the resultant of the rate of processes A-(1) and B-(1), which is dependent on the solubility of the protons in a given metal, but observations lead us to suppose that the desorption rate in processes A-(2) and B-(3) also plays an important role. The latter is dependent mainly on the catalytic ability of the surface of the metal to accelerate or retard the reaction of the formation of molecules from hydrogen atoms. Thus, for example, the presence of arsenic on the surface of an iron cathode retards this reaction and inhibits one of the stages of both the A and the B process (A-(2) and B-(3)). Arsenic, therefore, prevents the escape of hydrogen from within the iron cathode and raises the overvoltage on it.

The action of arsenic is weaker on the surface of nickel, since this metal is a good catalyst for the reaction in question. The presence, therefore, of nickel on the surface of an iron cathode accelerates the desorption process and lowers the rate of the penetration of hydrogen into the metal. The presence of polar organic substances in a solution causes — at certain sufficiently negative values of the potential — adsorption of the molecules of this compound on the surface of the cathode; this, in turn, causes a diminution in the rate of both process A-(1), and B-(1), in consequence of which there is an increase in the hydrogen overvoltage and a decrease in the rate of hydrogen penetration into the metal.

The above conception, which is based on the assumption that protons penetrate into the body of the cathode, seems thus to offer a logical, albeit only a qualitative explanation of the differences to be found in the value of the hydrogen overvoltage on different metals.

Verification of this hypothesis and also its quantitative argumentation will form the subject of further researches.

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CHEMISTRY

The Positive-Negative Azeotrope: Glycol—*o*-Cresol—2,4,6-Collidine. XXIII

by

Z. KURTYKA

Communicated by W. ŚWIĘTOSŁAWSKI at the meeting of November 28, 1955

Introductory remarks

No ternary, positive-negative azeotropes formed by a weak acid, a weak base and glycol, have yet been investigated.

First, the author examined the boiling temperature isobars of a series of binary systems formed by ethylene glycol G in combination with pyridine, 2,5-lutidine, 2,6-lutidine, 2,4,6-collidine respectively.

It was found that only 2,4,6-collidine P forms with glycol a positive azeotrope containing about 10% weight of glycol with an azeotropic depression of $0.8^{\circ}C$. All the other representatives of the pyridine bases lie beyond the azeotropic range of glycol.

According to Horsley's tables [1], glycol forms with *o*-cresol F an azeotrope containing 27% weight of G, and shows an azeotropic depression of $1.5^{\circ}C$. It was expected that glycol, *o*-cresol and 2,4,6-collidine would form a ternary saddle azeotrope $[(-)F, P(+)G]$. It seemed probable that the concentration ratio $P:F$ would be lower in the ternary azeotrope than in the negative one. This fact influences the position of the top-ridge line, as is shown below.

The purpose of this paper is to prove the existence of the saddle azeotrope and to determine the shape of the top-ridge line and the location of point $(\pm)Az$, corresponding to the composition of that azeotrope.

A detailed description of the purification of the components themselves and of the ebulliometric method of measurements will be given elsewhere [2].

Much care was taken to ensure the use of wholly dehydrated substances and their mixtures.

Ebulliometric method used

The concentration triangle is divided by the main line GC, joining point G which corresponds to pure glycol, to point C which represents the composition of the binary negative azeotrope.

In most of the cases examined until now in our laboratory, point $(\pm)Az$, corresponding to the composition of ternary saddle azeotropes, was usually found inside triangle GPC, in which the point representing the pure base and not the pure acid was found, whereas in the system under examination point $(\pm)Az$ was found inside triangle GCF.

The experiments consisted in establishing the shape of the boiling temperature isobars formed by mixing glycol with two other components: with 2,4,6-collidine and *o*-cresol separately on the one hand and with the negative azeotrope $[(-)F, P]$ on the other.

In addition, a series of boiling temperature isobars, represented in Fig. 1 by horizontal lines, had to be examined in order to find, by extrapolation, the minimum boiling point on the top-ridge line, representing both the composition of the saddle azeotrope and its boiling temperature.

The Świętosławski ebulliometric method was used for examining the ternary, positive-negative azeotropes [3].

Experimental part

For examination of the boiling-temperature isobars there was used a three-stage Świętosławski ebulliometer, so that the boiling temperature t_1 and the two condensation temperatures t_2 and t_3 were measured after each addition of small amounts of one mixture to another (e. g., mixture 1″ to 1′, Fig. 1). A simple ebulliometer filled with water served for determining small atmospheric pressure changes.

Results

In Table I are listed the boiling temperatures and the compositions of the binary azeotropes. In the first column (I) the boiling temperatures of the azeotropes are given, in the second (II) the composition of the azeotropes expressed in weight (a) and in mole (b) per cent of the higher boiling component, and in the third (III) the azeotropic temperature decreases or increases.

TABLE I

Binary positive and negative azeotropes

Name	(I)	(II) a	(II) b	(III)
glycol—collidine P	170.50	9.7	17.4	0.8
glycol—*o*-cresol F	189.52	26.0	37.98	1.48
o-cresol—collidine	197.20	63.0	61.80	6.20

In addition, the minimum boiling temperature on the isobar formed by mixing G with $[(-)F,P]$ was equal to 187.00° C.

The composition of that mixture was ~42% of glycol and ~58% of the negative azeotrope. The following boiling temperatures of pure components were determined: glycol 197.45° C, *o*-cresol 191.00° C, and 2,4,6-collidine 171.30° C. The thermometer was calibrated by the use of a precise, electric-resistance thermometer.

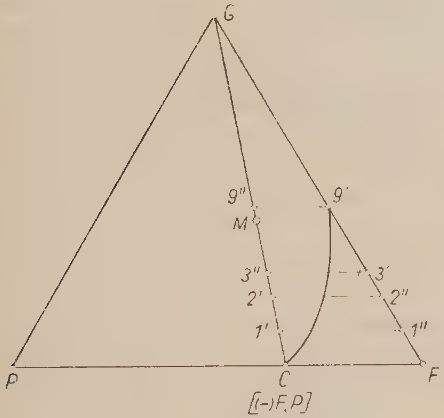

Fig. 1

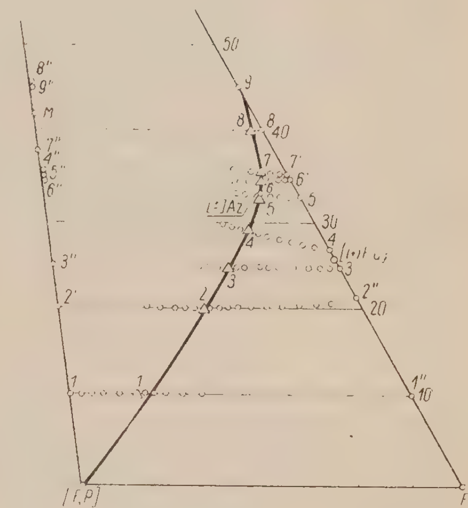

Fig. 2

Fig. 1. On the concentration triangle GFP the projections of the main line GC and of the sections $1'1''$, $2'2''$, ... $9'9''$, corresponding to the boiling temperature isobars of different ternary mixtures composed of glycol, G, orthocresol, F, and 2,4,6-collidine P, are shown.

Fig. 2. A portion of a concentration triangle, limited by points G, F and $[(-)F,P]$, is presented. The projections of the sections of the boiling temperature isobars are shown by the dotted lines. The shapes of the boiling temperature isobars were ebulliometrically determined by mixing $1'$ with $1''$, $2'$ with $2''$ and $7'$ with $7''$. The eight maxima found on these isobars lie on the projection of the top-ridge line and are represented by a small triangle.

In order to determine the position of the azeotropic point and the shape of the top-ridge line, the shapes of a series of sections of the boiling temperature isobars were examined. They are represented in Fig. 2. The results obtained are given in Table II and are shown graphically in Fig. 2.

It may be seen from the graph (Fig. 2) that the top-ridge line declines sharply from the main line GC and after reaching the composition of the saddle azeotrope $(\pm)Az$, merges with the side GF of the concentration triangle.

Because of minute temperature differences, the tridimensional shape of the surface of the boiling temperature isobar is, as usual, very flat. For this reason all the maximum temperature increases observed for mixtures represented by points lying on the top-ridge line are relatively small. This is evident from the data given in Table II in which the values characterising the nine isobar sections are given.

In this Table are listed: in column (I) — the respective boiling temperatures of the initial mixtures: 1′, 2′, 3′, 4′, 5′, 6′, 7′, 8′, and 9′; in column (II) — the composition of these mixtures expressed in weight per cent ($^0/_0 G$); in column (III) — the composition of the mixtures added, viz., 1″, 2″, 3″, 4″, 5″, 6″, 7″, 8″, and 9″; in column (IV) — the maxima of the boiling temperatures on the top-ridge line, in column (V) — the composition of mixtures characterised by the boiling temperatures given in column (IV), and in column (VI) — the boiling temperature differences found by subtracting values (IV) from the value obtained for the negative azeotrope [$(-)F,P$], namely: $t = 197.2^0$C.

TABLE II

Boiling-temperature isobar sections 1′1″, 2′2″ ...

No.	(I)	(II)			(III)			(IV)	(V)			(VI)
		$^0/_0 G$	$^0/_0 F$	$^0/_0 P$	$^0/_0 G$	$^0/_0 F$	$^0/_0 P$		$^0/_0 G$	$^0/_0 F$	$^0/_0 P$	
1	192.53	10.0	56.7	33.3	10.5	89.5	—	192.68	10.09	62.61	27.30	4.52
2	189.59	20.0	50.4	29.6	21.2	78.8	—	190.69	20.63	65.23	14.14	6.51
3	189.50	25.3	74.7	—	25.27	47.08	27.65	189.88	25.29	64.76	9.95	7.32
4	189.52	27.2	72.8	—	36.50	40.0	23.50	189.69	29.62	64.27	6.11	7.51
5	189.58	32.65	67.35	—	35.18	40.84	23.98	189.65	33.05	63.11	3.84	7.55
6	189.64	35.25	64.75		35.13	40.87	24.00	189.69	35.23	61.88	2.89	7.51
7	189.76	37.75	62.25		35.20	40.82	23.98	189.80	37.55	60.64	1.81	7.40
8	189.93	40.07	59.93		45.45	34.37	20.18	189.95	40.32	58.66	1.02	7.25
9	190.16	45.06	54.94	—	45.16	34.55	20.29	—	—	—	—	—

In order to verify the results obtained for the composition of the ternary saddle azeotrope $(\pm)Az$, a mixture containing $5^0/_0$ of P, $35^0/_0$ of G and $60^0/_0$ of F was submitted to fractional distillation. The main fraction was collected within 189.60—189.70^{0}C. The latter was characterised by the third degree of purity according to the ebulliometric scale [4] ($t = 0.045^0$). It contained $60^0/_0$ of the mixture put into the flask.

Its composition was: $4.0 \pm 0.7^0/_0$ of 2,4,6-collidine. The difficulties encountered in arriving at a precise determination of the glycol and *o*-cresol contents of the mixture made it impossible to obtain precise analytical data for these two components in the main fraction of the saddle azeotrope. The composition of that azeotrope was ascertained by

a graphical interpolation of the results found in the series of ebulliometric measurements as shown in Fig. 2 and in Table III.

TABLE III

Composition of the ternary positive-negative azeotrope

Component	Percentage by weight	Percentage by mole	Boiling temperature
2,4,6-collidine	4.0	2.86	189.65 ± 0.1°C
glycol	33.6	47.02	
o-cresol	62.4	50.12	

It should be added that the ternary saddle azeotrope is homogeneous both at boiling and at room temperature; therefore it is a homoazeotrope.

I wish to express my thanks to Professor W. Świętosławski for his help and advice.

Summary

1. The system here investigated is characterised by the fact that its top-ridge line lies in a triangle limited by points corresponding respectively to the negative azeotrope $[(-)F,P]$, to glycol G, and to *o*-cresol F.

2. In the vicinity of point $[(-)F,P]$ there is a very sharp decline in the boiling-temperature isobar of mixtures represented by points lying on the top-ridge line, whereas near the azeotropic points its shape becomes very flat.

3. The boiling-temperature isobar of the top-ridge line, after reaching its minimum, rises slightly, and merges with the side isobar glycol—*o*-cresol at a point corresponding to about 42% weight of glycol.

4. The top-ridge line has a different character in this system as compared with that in the ternary systems $[(-)Ac,P(+)H]$ which contains as the third component, not a polar substance, like glycol, but an aliphatic or aromatic hydrocarbon.

5. The composition of the ternary positive-negative azeotrope is as follows: 33.6% G, 62.4% F, 4.0% P in weight per cent; 47.02% G, 50.12% F, 2.86% P in mole per cent. Its normal boiling temperature is 189.65 ± 0.1°C.

6. The top-ridge line, on which the azeotropic point $(\pm)Az$ is found, is strongly curved towards the increasing content of the acid.

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GEOLOGY

New Stratigraphic Division of the Dogger, Based on Ammonite Fauna, in the Marginal Areas of the Holy Cross Mountains

by

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The Dogger of the Holy Cross Mountains consists of sediments from a markedly shallow sea which at that time encircled the elevated massif of these mountains. That complex had by then been upthrust as a peninsula stretching for some distance to the north. It constituted part of a continent expanding southward, and toward the close of the Middle Jurassic it was flooded by transgression. The shallow water provenance of the Dogger in the Holy Cross Mountains is suggested by the distinct predominance of rocks with an important admixture of the coarser fractions of terrigenous material — frequently the chief rock constituent — as well as by the great range of sedimentary facies noted even within small areas. Ripple marks, trails and the prevalence of molluscs in all the more organogenic rocks support this opinion. With comparative frequency, they form almost typical shell breccias of battered mollusc shells, with genus *Pseudomonotis* in greatest abundance. "Oystershell" limestones also occur, consisting mainly of minute *Ostrea*, and less frequently of thick-shelled *Gryphea*. Limestones of the Lowest Dogger carry fairly numerous casts of jelly fish *(Medusina gorgonoides)* deposited on sandy beaches. In the (same) lower series it has been possible to ascertain beyond doubt that deposits sedimented at an earlier time had been washed out, and that characteristic erosional cavities with an amplitude of several metres had been filled up by later sedimentation.

Inclusions of organogenic rocks, continuous over considerable areas, are, for the lithological stratigraphy of the Middle Jurassic, more significant in the north and east marginal areas. Among them are very peculiar arenaceous limestones showing a range of characters. Some resemble crinoidal limestones, others shelly limestones, or crystalline limestone with light-yellow or yellowish-ashy colouration. They present a most

interesting chemical composition, since, in addition to a fairly important amount of sand always found in these rocks, and the usual prevalence of calcium carbonate, they also, as a rule, carry varying amounts of magnesium and iron carbonates. In some parts of the rock, the two last-named even predominate over $CaCO_3$.

In the course of the Tertiary, arenaceous limestones, at that time close to the surface, were subjected to processes responsible for the withdrawing of the carbonates of calcium and magnesium and for the reduction of those of iron into oxides. Hence it is that, in exposures, only sands cemented by iron oxides are encountered, instead of the carbonic rocks here mentioned. These residual rocks are usually strongly porous and brittle, but in some places have retained the original texture and bedding of arenaceous limestones, and occasionally even the organic fossil remains contained in them. They have yielded an abundance of molluscs and even ammonites. All these characters, widely spread though not constant over the entire area under consideration, help to elucidate the marked differentiation in the appearance of these rocks presented in outcrops and close to the surface, or deeper down along their dip. This differentiation has led some investigators into error, making them suppose that the rocks were referable to various horizons, whereas they constitute a single horizon differentiated through secondary processes.

From the stratigraphic viewpoint, it is significant that arenaceous limestone and derivative rocks do not occur in the lower part of the Dogger but in the central part, make their appearance almost simultaneously over the whole of the east and north marginal areas, from the vicinity of Ostrowiec on the Kamienna stream as far as Żarnów near Opoczno.

The arenaceous-limestone facies recurs twice. First in the Middle Dogger ("lower arenaceous limestones") and again in the Upper Dogger ("higher arenaceous limestones").

The range of these two horizons is not, however, uniform; the lower arenaceous-limestone layer has developed throughout the entire area under discussion, while its upper layer occurs only in some of the more southerly portions.

The determination of the stratigraphic column of the Dogger in the Holy Cross Mountains was made possible by detailed studies of a score of sections in outcrops of the Middle Jurassic series. It was also based on the lower boundary of araneceous limestones or that of equivalent exposed rocks subjected to secondary metamorphism, considered as the type-horizon. Roughly outlined, with the omission of numerous local details and changes, the scheme in descending order would be as follows:

D - Upper arenaceous limestone series or its stratigraphic equivalent showing a different facies. i. e.

Upper sands and sandstone series intercalated by argillaceous sandstones and mudstones.
Depth of series approx 100 m.;

C — Lower arenaceous limestone series with an argillaceous intercalation in the roof (from a few to a score of metres thick).
Total depth of series from 20 to 50 m.;

B — Lower argillaceous series divided into the upper and the lower part by intercalations of sandstones.
Total depth of series from 150 to 180 m.;

A — Basal sandstones, in the upper part, moderately coarse-grained and ferrous, in the lower part fine-grained, white or yellowish-white.
Thickness ranging from a few to several scores of metres.

Thus far, the A Series has not been consequently differentiated. Its lower part has as a rule been still referred to the Lias, sometimes even including its upper part. Only occasionally, when separated from the Lias, has the latter part been correlated with the Lower Bajocian on groups of resemblance with the so-called "Kostellitzer sandstones" of F. Roemer (1870). Interbedding sandstones from the B series have also occasionally been referred to the Lias.

The lower part of the lower argillaceous series (B) used to be referred to the Bajocian, the higher part to the Bathonian, while both the upper series (C and D), as a rule studied together, used to be assigned to the Callovian, partly even the Oxfordian age.

The division of the Dogger in the east and north marginal areas of the Holy Cross Mountains has thus far been determined on very scanty fauna, as time-marker for regional stratigraphy, mainly on the evidence of analogies of lithology with areas even quite far distant. Polish geological literature contains but few references concerning the occurrence in the Holy Cross Mountains of certain specimens of ammonites, thus far identified as *Parkinsonia* sp. or *Parkinsonia parkinsoni*.

Lewiński (1901) did not, during his research work on the Jurassic from the Holy Cross Mountains, discover a single identifiable ammonite in the Dogger of that area.

Samsonowicz (1928, 1934) records parkinsonians from Wyszmontów and Jedlanka and from a road-cut to the north of Lubienia; those found at the last named locality were *Park. parkinsoni*. Passendorfer (1922, 1928, 1930, 1939) recorded parkinsonians from Szarbsko, Gielzów and the vicinity of Inowłódz, but he does not identify them specifically. In addition to these authors, Kuźniar (1927) also mentions that rocks from Parczów "carry a fauna containing *Park. parkinsoni*".

In 1939, the author published a preliminary report on the discovery in arenaceous limestones from the neighbourhood of Jastrząb, of the

first specimens of parkinsonians. Later (in 1949), he reported the occurrence in these rocks of *Park. schoenbachi* and *Park. eimensis*, confirming their Vesulian age.

The author has collected and described 27 specimens of ammonites from the lower and middle Dogger. Another specimen was found by him in the old collections of the Institute of Geology at Warsaw University, while two more parkinsonians and one garantiana of great value were presented by his colleagues, Prof. R. Krajewski, M. Kobyłecki and W. Karaszewski.

From that scanty collection of Middle Jurassic ammonites, so modest yet far outnumbering the total of ammonite specimens ever previously found in the Holy Cross Mountains, a dozen or so seemed more exactly identifiable and sufficiently interesting to justify further investigation. The greater part of them were referable to species, and in some cases to genera never recorded from that region, or even not at all known from the Jurassic uplands of the south of Poland or even throughout Poland.

The collected ammonite fauna comes from various Dogger series and gives a clue to their correlation.

The oldest series of basal sands and sandstones from Orłowo near Jastrząb have yielded a fair abundance of ammonites, namely *Strenoceras subfurcatum* var. *oolithicum* Qu., *Strenoceras* sp. (cf. *subfurcatum* Ziet) and *Apsorroceras cylindricus* Baug & Sauz, confirming that the bottom sectors of these series are referable to the lower Vesulian. The middle layers of these sandstones from the vicinity of Małachów near Petrykozy have also yielded the lower Vesulian species *Subgarantiana subangulata* Wetz. These specimens, though recorded from localities lying some distance apart, all suggest the absence from the north and east marginal areas of the Holy Cross Mountains of the strict Bajocian, i. e. older than the *Strenoceras subfurcatum* horizon, and of marine facies deposits assignable to that period. The Middle Jurassic transgression, cutting the discordantly disturbed lower Lias, did not commence here before the beginning of the lower Vesulian *).

Analogies with the "Kostellitzer Sandstein" from the Częstochowa region may here be drawn as regards the facies of the basal sandstone series only. Similarities in lithology and the general character of the faunal assemblage are now and again very notable indeed. The two series are, however, obviously of different age.

As shown in this writer's ealier paper (1953) the "Kostellitzer Sandstein" bear an upper Aalenian fauna, that is, *Tmotoceras* sp., *Ludvigella* sp., *Variamussium pumillum*, etc. and forms of the lower and middle Bajocian such as *Soninia sowerbyi*, *Inoceramus polyplocus*, etc., while

*) The stratigraphic column drawn up by the author has been published in [1].

the overlying chamosite sandstones are referable to the upper Bajocian *(Toeloceras humphresi, Toeloceras blagdeni)*; basal sandstones from the Holy Cross Mountains all belong to the lower Vesulian; the sands and ferrous ferruginous sandstones with facies approaching that of the "Kostellitzer Sandsteine" are referable even to higher parts of that sub-stage.

The lowest layers of the lower argillaceous series still contain a fauna from the uppermost part of the lower Vesulian *(Subgarantiana suevica)*, while parkinsonians from the *Parkinsonia parkinsoni* group make their appearance somewhat higher up.

Sandstones intercalating the lower argillaceous series carry an index middle Vesulian fauna, discovered by Samsonowicz (1928) near Lubienia and later confirmed by the present author (1949), that is, *Parkinsonia* cf. *parkinsoni*, *Astarte* cf. *depressa*, *Trigonia* cf. *clavellata*, etc.

A rich ammonite assemblage comes from the higher part of the lower argillaceous series. It is represented in a rich fauna from Parczów containing: *Park. subarietis*, *Park.* cf. *parkinsoni*, *Park. friederici-augusti*, *Park.* cf. *pseudoparkinsoni*, *Park. depressa*, *Park. depressa* var. *robusta*, *Park. neuffensis* and *Park. ferruginea* var. *dorni* nov. var. — the last one altogether different from the true *Park. ferruginea* from the upper Vesulian [2].

Probably, the uppermost part of the lower argillaceous series actually belongs to the highest middle Vesulian horizon (*Park.* aff. *radiata* from Koryciska).

The index ammonites of the *Park. schloenbachi* horizon, however, make their appearance higher up, in the lower layers of the lower arenaceous shelly limestones. Various forms of *Park. schloenbachi*, such as *Park. schloenbachi* Schlippe and *Park. schloenbachi Dorn*, non Schlippe, also *Park. eimensis* come from a number of localities: Zastronie, Zakościele near Inowłódz and Dęborzeczka.

The higher beds of the arenaceous shelly limestones have yielded a *Parkinsonia* specimen, the determination of which oscillates between *Park. württembergica* and the index form of *Park. ferruginea*. Both determinations of this specimen are of almost equal stratigraphic significance, suggesting that this portion of the arenaceous shelly limestones is already referable to the Vesulian.

It is noteworthy that both the last mentioned *Park. württembergica-ferruginea* and the *Park. schloenbachi Dorn* (non Schlippe) have been found in ferruginous ferrous rocks which had experienced secondary metamorphism and outcrop in exposures of the lower shelly arenaceous sandstones.

The higher arenaceous sandstone series and other deposits equivalent as far as facies is concerned, contain an abundant fauna of molluscs and brachiopods bearing distinctly Bathonian characters: *Rhynchonella alemanica*, *Rh. feorryi*, *Rh. concinna*, *Burmirhynchia* sp., *Acantho-*

thyris spinosa and *Chlamys ambigua*, *Chl. dewalquei*, *Entolium ryphaeum*, *Cucullea clatrata*, *Cuc. concinna*, *Astarte cordata* etc.; even so, they have not supplied an identifiable ammonite fauna.

Nevertheless, not all the arenaceous limestone series belong to the Bathonian. Within its upper part, from Mt. Sowia Góra near Cmielów, Samsonowicz (1934) collected certain undoubtedly Callovian specimens, some of which the present author had the opportunity to identify. Among them are such unquestionably lower Callovian species as *Macrocephalites tumidus*, *Hecticoceras pompecki* and *Phylloceras* aff. *kudernatschi*. Lower Callovian fauna were also found by the author in the roof parts of the upper arenaceous shelly limestones from the vicinity of Swiniów to the north of Jastrząb.

From that upper arenaceous shelly limestone complex, however, almost one hundred metres thick, not more than a layer a score or so metres thick is assignable to the lower Callovian, while the main rock mass of this series is doubtlessly referable to the Bathonian Upwards from the upper arenaceous limestones the facies changes are most marked. The upper Callovian, represented by a very rich ammonite fauna (over 200 specimens) from Świnna near Opoczno (Różycki 1939), has developed as grey, pink and greenish glauconitic marks and marly limestones with an insignificant admixture of terrigenous material. The lithological character of the rocks and the faunal assemblage from these beds resemble the so-called Glauconitic Beds of the Częstochowa region. Studies of fauna from Świnna (Różycki 1939) indicate that in the nothern Holy Cross Mountains area there are represented not only all the three upper Callovian horizons but also the lower Divesian.

The upper Divesian, developed in a marly facies, passes upward to alternating series of marly limestones and whitish-grey marls containing all the Nevisian fauna not differentiated from that in analogous beds of the Częstochowa Jurassic series. In the same way, Argovian plate limestones and the fauna they contain show complete similarity with the Argovian near Częstochowa and Cracow.

The study of ammonite fauna from the Dogger of the Holy Cross Mountains, and the stratigraphic column determined thereby, suggest the following not unimportant conclusions:

1. The Dogger transgression in the Holy Cross Mountains is much younger than that in the Częstochowa region. In connection therewith, the composition of the lower members of the Dogger in these two regions is not the same, despite certain facial similarities shown in parts of the profile.

2. The two arenaceous shelly limestone series, thus far both assigned to the Callovian, are of different ages. The lower series belongs to the upper, partly to the middle Vesulian, the upper series to the Bathonian.

3. Suggestions previously based on direct geological observations (1939) have now been confirmed by paleontological and stratigraphic evidence, namely that ferruginous ferrous sands are a product of secondary modifications experienced by arenaceous shelly limestones during the Tertiary, and that their occurrence is connected with the old surfaces of that period. Ferruginous ferrous sands do not form isolated stratigraphic horizons within the Dogger, but are connected with outcrops of arenaceous shelly limestone in the upper Vesulian and the Bathonian.

4. The facial development of the Holy Cross Mountains Dogger series differs markedly from that in the Częstochowa area, but displays considerably more features common to those of the middle Jurassic in the Kujawy region.

REFERENCES

[1] S. Z. Różycki, *The Upper Dogger and the Lower Malm of the Kraków-Częstochowa Jurassic*, Prace, Instytut Geologiczny, Warsaw, 1953.

[2] — *On Some Parkinsonia, Garantiana and Strenoceras...*, Acta Geol. Polon. **5** (1955), 114.